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## EDITOR'S NOTE

It is very much regretted that owing to circumstances beyond our control, it has not been possible to include in the present volume chapters on Pesticides, Adhesives and Enzymes. These omissions will be rectified in the next volume.

It should also be stated that as the literature is becoming so voluminous, it has been decided as a matter of policy, in order to keep the size of the volume within reasonable limits and to give a better assessment of progress in subjects where development is slow, that certain chapters will be included only in alternate years.

# INORGANIC CHEMISTRY





## MINERALOGICAL CHEMISTRY

By W. H. BENNETT, M.Sc., F.R.I.C.

*(Overseas Geological Surveys)*

### Supply of ores and minerals

A REVIEW of the world mining industry for 1960 (1) emphasises the rapid increase in mineral production in the countries of the Communist bloc, especially China. This has not affected world markets as much as was expected, owing to the heavy internal industrial demand, which might possibly exceed the increased production and necessitate the working of lower grade ores. The metal user is often able to use alternative materials in the face of shortage or rising prices, so that there is little possibility of absolute mineral shortages developing.

### Aluminium (1, 2)

The production and consumption of aluminium is increasing, after a setback in 1957-58, but potential supply still exceeds demand and a significant proportion of production facilities are still idle. Large deposits of bauxite, some of low grade, are reported to be under investigation in Jamaica and British Guiana, and the deposit on Cape York Peninsula, Queensland, is now stated to consist of 2000 million tons of possible commercial grade material.

A report (3) on the Arkansas bauxite region, the most important occurrence in the U.S.A., gives an account of detailed investigations begun in 1941 as part of a study of the bauxite resources of the U.S.A. Reserves in 1950 were estimated at 70.7 million long tons averaging  $\text{Al}_2\text{O}_3$  50% and  $\text{SiO}_2$  9%, and numerous analyses are published. The principal ore mineral is gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) and the main impurities kaolinite, siderite and iron and titanium oxides. A study was made of the distribution of the minor elements in the bauxite and source rocks (two varieties of nepheline syenite). The average niobium content of the bauxite was 0.05%.

A process has been described (4) for recovering cell-grade alumina from aluminiferous shale which is decomposed with hot  $\text{H}_2\text{SO}_4$  and then leached with hot  $\text{K}_2\text{SO}_4$  solution. Cooling precipitates potash alum, which is purified, ignited and leached with water, to give a residue of pure  $\text{Al}_2\text{O}_3$ . The  $\text{K}_2\text{SO}_4$  and most of the  $\text{H}_2\text{SO}_4$  is recoverable.

### Uranium (5-8)

Uranium ore production in 1959 was the highest so far: the Free World produced over 43,000 tons of  $U_3O_8$ , the U.S.A. leading with 16,390 tons, closely followed by Canada with 15,910 tons. The future demand is uncertain and reserves continue to increase. The introduction of nuclear power is slower than was once expected and the demand for uranium is unlikely to build up again until some time in the 1970s. The U.S. Atomic Energy Commission has decided not to exercise its option to purchase Canadian  $U_3O_8$  when the present contracts expire in 1962-63 but has agreed to extend deliveries until 1966. Canadian mining companies are to undertake a joint research programme to discover new uses for uranium.

### Diamonds and gemstones

Sales of industrial *diamonds* continue to increase. Development continues in the Yakutsk diamond field in the U.S.S.R. and the old diamond field of the Urals has been extended by improved prospecting methods. The total output of synthetic diamonds by the American General Electric Co. (G.E.C.) in 1959 was stated to be  $2\frac{1}{2}$ -3 $\frac{1}{2}$  million carats against a world output of about 20 million carats of natural industrial diamonds. The synthetic material is only suitable for use in resin-bonded grinding wheels. The Congo is by far the largest producer of industrial diamonds and, in view of recent developments in that country, the statement that De Beers have succeeded in producing synthetic diamonds is of interest.

A review of diamond mining practice in South Africa has appeared (9). The success of the mechanical concentration methods employed is surprising, as it represents a concentration ratio of about 20 million to one. Alluvial diamonds were found in Sierra Leone in 1930, and a dyke of claylike material carrying diamonds found in 1948. From this and other similar dykes, borehole cores of unweathered kimberlite have been obtained comparable in chemistry and mineralogy with South African kimberlite (10).

The results have been published of X-ray crystallographic and spectrographic examination of synthetic diamonds from the American G.E.C. and the Swedish A.S.E.A. (11). The former always contain single-crystal inclusions of nickel or of a nickel-rich face-centred cubic compound. The Swedish diamonds do not contain nickel and are generally less well crystallised. A communication from the American G.E.C. (12) outlines the systems studied in connexion with diamond synthesis. These included (a) direct transition, graphite to diamond, (b) systems involving carbon and oxygen, (c) those containing salt-like carbides, (d) miscellaneous chemical reactions, and (e) carbon dissolved in molten metals. The last were the most fruitful and the catalyst metal could be Cr, Mn,

Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt or Ta. Pressures used ranged from 55,000 to 100,000 atm. at 1200°–2400°.

*Pearls* are usually classed as gemstones and an account has been given (13) of the production of cultured pearls in Japan, which has increased steadily in value since 1951. In 1958 exports totalled nearly U.S.\$17 million, over \$10 million going to the U.S. A nucleus consisting of a round mother-of-pearl bead, made from fresh-water mussel shell, is inserted into a 3-year pearl oyster. Three to four years' growth under favourable conditions is then required for the formation of a medium to large pearl.

### Miscellaneous

A survey of the *beryllium* industry has been published (14) dealing mainly with the production and resources of beryl in the U.S.A. Heterogeneous pegmatites are almost the only source of beryl. Although reasonable supplies of ore are available and demand for the metal has grown steadily, more rapid developments will depend on the solution of metallurgical problems and a reduction in price.

Interest has been sustained in sources of *niobium*, including extensive deposits containing pyrochlore, often of relatively low grade. The only commercial producer of pyrochlore in 1959 was still the Söve plant in Norway, but pilot plant tests have continued at Panda Hill, Tanganyika, and it has been reported that exploitation is planned of possibly the biggest pyrochlore deposit in the world at Araxá, Brazil. An important book by G. L. Miller deals with the occurrence, extraction, metallurgy and applications of tantalum and niobium (15).

The increased demand for *titanium* dioxide for pigments is encouraging for ilmenite producers, but slowness in the development of a demand for titanium is reflected in the price of rutile, which fell from over £100 a ton three years ago to £28 in March 1960, and a number of Australian producers have ceased work.

The bulk of the world's known reserves of *tungsten* ores is in Communist areas, notably in China, where reserves are estimated to contain 1 million tons of tungsten. By contrast the U.S.A. has 70,000 short tons and other countries even less. An important deposit of scheelite averaging  $\text{WO}_3$  2.18% has been found in Canada in the McKenzie Mountains and a development programme has been announced. Although recently in over-supply, potential uses of *molybdenum* and tungsten may result in a critical supply situation in 10–15 years. An extensive deposit of molybdenite, estimated to contain 5 million tons of Mo, was reported in North-East Sardinia and, if developed, this should be an important factor in world supplies (16).

The Rio Tinto–Dow thorium plant at Elliot Lake, Ontario, which uses a solvent extraction process to recover *thorium* from the

liquors remaining after uranium extraction, was brought into production in 1959 with a capacity of 150 tons of  $\text{ThO}_2$  per annum and may affect other producers. The South African monazite mine, the largest producer of monazite in recent years, closed down early in 1959, and the Indian rare-earths factory was shut during most of 1959.

An account has been published of the mining of celestine, the principal commercial source of *strontium* salts, at a deposit producing 90% of the world's output near Chipping Sodbury, Gloucestershire (17). A book by D. W. Kaufmann (18) gives a comprehensive account of the production of *common salt*, including sections on the mineralogy, geology, U.S. deposits, solar production from sea water, technology and industrial uses. A third edition has appeared of a comprehensive reference book on the mineral industry giving much general information on the production, industrial uses and resources (more especially in the U.S.) of non-metallic industrial minerals and rocks (19).

The proceedings have been published of a symposium reviewing the mineralised areas of Great Britain and Ireland and the economic problems bearing on their exploration and development (20). It was suggested that the decline of the flourishing metal industry of 100 years ago was not entirely due to exhaustion, and that some revival could take place by utilising modern methods of exploration and a revision of the mining tax structure.

### Analysis

#### *Field methods for the detection of beryl*

The search for commercial deposits of beryl, which are difficult to recognise in the field, has been assisted by the development of rapid chemical field tests. Dressel & Ritchey (21) fuse the powdered sample with an alkaline flux in a wire loop, dissolve in water and detect Be (sensitivity about 0.01%) by the fluorescence with quinzarin. McVay has recommended a qualitative field test for Be in which duplicate samples are fluxed, one with  $\text{KHF}_2$ , the other with  $\text{KHSO}_4$ . Aqueous extracts are made alkaline, morin added and the fluorescence in the short-wave ultra-violet region compared with that of an authentic sample containing beryl (22). Wells *et al.* put forward a method for use in geochemical prospecting studies in which the sample is fused with ammonium fluoride and extracted with dilute  $\text{HNO}_3$ . Interfering ions are complexed and Be estimated by the berillon colour in alkaline solution (23).

Brownell (24) describes a portable Be detector ('Beryllometer') based on the  $(\gamma, n)$  reaction with a  $^{124}\text{Sb}$  source. This employs a scintillation counter to record the neutrons produced. Bowie *et al.* (25) use the same reaction but with  $\text{BF}_3$  counters to detect and measure the neutron flux. Both methods permit rapid determinations *in situ* and greatly expedite prospecting for Be minerals.

*Silicate analysis*

As analysis of kyanite for the U.S. Government stockpile by different laboratories had shown varying results, a large, carefully taken sample was split and sent to seven laboratories in the U.S.A., U.K. and Kenya, and the results obtained are summarised (26). The main errors were in the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  determinations, due to incomplete recovery of  $\text{SiO}_2$  after two acid evaporations, and incomplete ignition of  $\text{Al}_2\text{O}_3$ , which should be given 1 h. at  $1200^\circ$ . There is still a great need for an accurate direct method for the determination of  $\text{Al}_2\text{O}_3$ .

Jeffery & Wilson (27) describe a method for determining  $\text{SiO}_2$  in rocks and minerals by removing most of the  $\text{SiO}_2$  by one evaporation with HCl and determining the remainder by a photometric molybdenum blue method. Large amounts of Ti, Fe or P interfere, although Ti and Fe are easily removed. The same authors (28) have described a modified method for determining water,  $\text{CO}_2$  and carbon in silicate rocks with a closed-circuit system, in which air is re-cycled, whereby considerably reduced blank values are obtained.

*Spectrographic methods*

(a) *Emission*.—An account has been published (29) of the methods recently used by the U.S. Bureau of Mines for the spectrochemical analysis of rocks, minerals and ores. A stabilised d.c. arc source is used with cupped graphite electrodes, matrix effects being reduced by dilution with a common base material. Owing to the complexity of the samples examined a total-energy method is used.

Ahrens and collaborators (30, 31) have investigated the combined use of ion-exchange enrichment and spectrochemical analysis in the determination of trace elements in silicate rocks, including Au and the Pt metals. Large samples can be worked up after HF attack in a Teflon beaker. Brooks (32) has used a similar method for the estimation of trace elements in sea water and has achieved enrichment factors of up to  $2 \times 10^7$ . The abundance of Bi, Au and Cd in sea water has been determined in this way.

(b) *X-ray fluorescence*.—Molloy & Kerr describe instrumental improvements and the use of helium for the instrument path which have extended the range of this technique to the lighter elements (atomic No. 22–12), but consider that matrix and inter-element effects limit the method to semi-quantitative work (33). Hower (34) has applied matrix corrections in the trace element analysis of rocks and minerals, either by the calculation of mass absorption coefficients for major constituents if the proportions of these are known, or by the use of internal standards.

Solution techniques have been found to have some advantages, as matrix effects can be eliminated by dilution, although with a

loss of sensitivity, or internal standards can be added (35). Cullen (36) found that X-ray fluorescence methods could not be used directly for the determination of copper in mattes and slags, because of the absorption and enhancement effects of the matrix, but rapid and accurate results were obtained by fusing the sample with  $\text{KHSO}_4$  and grinding and briquetting the fusion to give a uniform surface for exposure. A rapid routine X-ray fluorescence method has been described (37) for the determination of Al, Si and Fe in clay or bauxite, using synthetic standards of oxide mixtures. Webber (38) employs X-ray fluorescence methods for the rapid analysis of soil samples in geochemical prospecting. For most purposes direct examination of the sample in a plastic holder is sufficient, but increased sensitivity is obtained by acid extraction and evaporation on filter paper.

### Geochemistry

'Methods in Geochemistry', edited by Smales & Wager (39), deals with the chemical, spectrographic, mass spectrographic, radiochemical and other methods used to provide accurate analytical data for geochemical studies. The Geochemical Society is publishing *Geochemistry*, an English translation of the Russian journal *Geokhimiya*, which covers a similar field to *Geochim. cosmochim. Acta*. The literature of this subject, which may often appear academic, but has many practical applications, has grown considerably in recent years.

Studies of the trace elements of the two standard rocks G-I and W-I are still yielding useful results, and additional data have been reported for Cd (40), Au (41), Ag and Tl (42), La and Sc (43), Se and V (44, 45), Sr (46, 47) and Ta (48).

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## ACIDS, ALKALIS AND SALTS

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### Sulphur and its compounds

#### *Sulphur*

World consumption of sulphur rose to a new record level of 16.1 million tons in 1959, an increase of about 5% over the figure for 1958. A further increase of about 5% is expected in 1960 (1). Although U.S. production declined slightly in 1959—to 6.11 million tons—exports continued to increase, totalling more than 1.6 million tons in 1959, and almost equalling the record of 1956 (2). World output of sulphur still exceeds consumption, however, and there is some overcapacity (3). In the U.K., consumption in 1958 fell somewhat to 1.078 million tons (4), but has since risen again. The accelerating downward trend of prices continues to cause alarm, especially amongst the smaller producers (5).

In contrast to the poor position in most parts of the world, where output declined owing to lack of demand, the production of sulphur from native ores is believed to be rising in mainland China, the overall output in 1958 having been estimated at as much as 150,000 tons (6); much of this was exported to the U.S.S.R. but some went to other countries, including Australia (7).

The difficulties experienced by the Italian and Sicilian sulphur industries in recent years have continued and there have been several plans to modernise the industry (8) in an attempt to combat the effects of competition from Lacq recovered sulphur, which is being produced in ever-increasing amounts (9). The position in most other parts of the world shows little change, although there is a tendency for the U.S.A. to lose markets in favour of Mexican and Lacq sulphur. An interesting development in Mexico was the opening of the world's first offshore mine (10), operated by the Freeport Sulphur Co.; an undersea pipeline is used to transport a maximum of 1500 tons of sulphur daily from the mine to the shore 7 miles away (11).

A bright future has been forecast for the Canadian sulphur industry (12), especially for sulphur recovered from sour gas (13). A new process here is the production of sulphur from high-quality roaster gas from iron ore smelters. The  $\text{SO}_2$  content of the gases is reduced with natural gas, now available locally at Copper Cliff,

Ontario, or with propane or fuel oil, at moderately high temperatures over a special catalyst, the composition of which has not yet been revealed (14). The companies concerned have developed the process because of the difficulty in marketing locally the liquid sulphur dioxide and sulphuric acid which would otherwise be produced.

A new liquid process for removing hydrogen sulphide from all types of gases, leaving less than 0.1 p.p.m. of this gas in the outgoing stream, with the production of pure sulphur, is known as the Stretford process. It is claimed to be effective for all concentrations of hydrogen sulphide, from the pure gas to traces only. The gas is brought into contact with a solution of the sodium salts of certain anthraquinonedisulphonic acids, with which  $H_2S$  reacts to give the corresponding hydroquinone and free sulphur. The hydroquinone is then re-oxidised to the quinone form, the whole process being cyclic (15). Interest has also been renewed in an old patented process (16) in which an organic dyestuff such as methylene blue is used as the oxygen carrier. The process has been developed by workers of the South Eastern Gas Board and is now being used on the semi-plant scale, after successful operation of a pilot plant. Aniline is used as solvent for the dyestuff and contact between the gas and solution is achieved in a packed column absorber. After treatment, the sulphur obtained is 99% pure (17).

Important deposits of sulphur were discovered recently in Poland (18) and are now being exploited, while there have been negotiations between the Iraqi Government and the Texas Gulf Sulphur Co. about possible exploitation of extensive sulphur beds in Iraq (19). Texas Gulf Sulphur have made progress in sulphur transport; they are now shipping molten sulphur in ocean-going vessels (20). A further development of interest is the formation of an International Sulphur Institute by manufacturers (21); the aims of this institute are to co-ordinate research on the handling, uses and marketing of sulphur (22).

#### *Sulphuric acid*

This acid has long been recognised as the barometer of the chemical industry and consumption suffered as a result of the recent recession; it has recovered and has now reached a new peak in the U.K. Thus, during the first six months of 1960, production of sulphuric acid and oleum (as 100% acid) was almost 1.34 million tons, 11% more than in the first half of 1959. The fertiliser industry is still the largest consumer, taking about 34% of the total, but the percentage of total output which is used in this industry is falling. The second major consumer of sulphuric acid is the titanium dioxide industry, which now uses about 17% of all sulphuric acid consumed in this country (23); this industry maintains a steady rate of growth, accounting for two of the five new acid plants known

to have come into operation during the past two years (24), with at least one other nearing completion. One of these plants produces sulphur dioxide for sulphuric acid manufacture from by-product ferrous sulphate. The dried sulphate is decomposed with coal in a fluidised bed roaster and the sulphur dioxide is then converted to trioxide for acid production in one of the existing converters. The residue is relatively pure iron oxides, which can be used in the steel industry (25).

### Caustic soda industry

World production of both caustic soda and chlorine set new records in 1959, at 10.2 and 7.2 million tons respectively. The constant demand for more chlorine, especially for the manufacture of other chemicals, has led to great changes in the industry. While 50% of world caustic soda output was made by the caustification of soda ash in 1950, only 33% came from this process in 1959. In the U.S.A., the trend in favour of the electrolytic process was even more pronounced than in the world as a whole, only 10% of the caustic soda output coming from the lime-soda process in 1959. These figures and an area breakdown of world capacity were reported at a congress held in Barcelona (26).

The platinised titanium electrodes recently developed by Imperial Chemical Industries Ltd. should prove of use in the electrolysis of brine. They show great resistance to erosion, so that their use precludes the necessity of adjustment to maintain the minimum electrode gap required for efficient operation. They have several other advantages over the conventional graphite electrodes (27). During the past year, silicon and germanium rectifiers have found increasing application in the field of high-power supplies for the electrochemical industry, notably in brine electrolysis. They give higher efficiency and reliability than earlier methods (28).

Two new processes have been developed recently for the concentration of caustic soda. In one, which has been in operation since 1958, 73% caustic solution at 260°F passes upwards through 20-ft. tubes in a heat exchanger while molten salt at 750-800°F passes downward through the shell. Anhydrous 99.8% caustic soda continuously discharges at 710°F to a flaker or drum packer (29). In the other, it is believed that a great saving in investment is accomplished by substituting long-tube vertical evaporators for Dowtherm heating, which has been used since 1946 (30).

### Sodium salts

#### *Sodium chloride*

Large new deposits of rock salt have been found in the Cheshire Basin. The salt lies in two beds, separated by rather more than 1000 ft. of marl, and reserves are estimated at about 400,000

million tons (31). A process for upgrading rock salt depends on an entirely new principle, based on the different heat absorption properties of the sodium chloride and the impurities in the rock salt. The ground material passes on a conveyer belt, coated with a heat-sensitive plastic material, under a source of infra-red radiation. The salt falls into a collector at the end of the horizontal traverse while the coating retains the impurities, which reach a higher temperature than the pure salt but are released as the belt cools on its return traverse (32).

Schreiber (33) describes the new Stockbarger fully-automatic apparatus for the production of salt monocrystals with melting points up to about 1350°. The equipment consists of a sinter carborundum crucible, which is heated to the required temperature, regulated to within 0.02°. The rock salt crystals formed are said to show no noticeable dispersion in ultra-violet rays. In a new process for the prevention of caking in sodium chloride, the deposition characteristics of the reprecipitated material are modified by adding a substance which gives multivalent complex anions in aqueous solution, thus preventing the formation of strong bonds between the original crystals (34).

#### *Sodium carbonate and bicarbonate*

In the U.S.A. soda ash output reached 5.61 million lb. in 1959, having recovered from the recession, and is expected to be even higher in 1960. There is a growing trend away from the use of synthetic processes towards refining natural deposits (35).

### **Halogens and their compounds**

#### *Chlorine*

With the increasing demand for chlorine, there has been renewed interest in chemical methods for its manufacture, other than the electrolysis of brine, which leads to excessive production of caustic soda if all chlorine requirements are met by this process. In Eastern Germany, Hennig (36) has studied former manufacturing processes, and has developed a modified Deacon contact process which can transform oxygen and excess gaseous hydrogen chloride quantitatively at a fairly low temperature. Work is continuing on the manufacturing technique but the product already obtained is stated to be satisfactory in all its properties. Electrolytic processes other than those involving brine electrolysis and those in which chlorine is formed as a by-product, as in the production of alkali and alkaline earth metals from their fused chlorides, include recovery of chlorine from by-product hydrogen chloride by the de Nora electrolytic process, which gives 99.9% chlorine and pure hydrogen as the only products (now in operation in the U.S.) (37), and one invented by Schroeder involving the electrolysis of nucleous

chloride produced by the action of by-product HCl on nickel. It is estimated that the costs of this process compare favourably with those of the de Nora process (38). Such processes are important, since large quantities of by-product hydrogen chloride are formed in organic chlorination reactions and, unless used in some way, present a serious disposal problem. A valuable booklet dealing with the history, methods of manufacture and uses of chlorine was published by CIBA Ltd. during 1960 (39).

#### *Hydrochloric acid*

In the U.S.A., newer processes for making hydrochloric acid are fast replacing the salt and sulphuric acid method. Several plants based on the older process have shut down and others are expected to do so. During the first eight months of 1959, production of the acid by this process declined, whilst that made from chlorine and hydrogen increased 15% and from by-product sources more than 35% (40).

In Israel, there is interest in the production of hydrochloric acid from the magnesium chloride of the Dead Sea brines by a thermal method. In this, the salt is hydrolysed, using a spray technique, in a directly heated furnace. The process is also applicable to the recovery of hydrochloric acid from spent pickle liquors and other chloride effluents and is being used for this purpose in the U.K. (41). In Germany, Badische Anilin- u. Soda-Fabrik A.-G. have developed an adiabatic absorption process for making hydrochloric acid economically from gases of any kind containing hydrogen chloride. Within a short time 60 plants using this process have been established all over Western Europe (42).

The problem of transporting anhydrous hydrochloric acid has received attention in the U.S.A., where tank cars with a capacity of 89,300 lb. of anhydrous acid cooled by two carbon dioxide tanks, each with a capacity of 730 lb., have been tested as a possible means of resolving the problem. The provision of safe, economic tankers has, hitherto, been impracticable (43).

#### *Oxyacids of chlorine and their salts*

Despite the introduction of alternative materials, sodium hypochlorite solution is still used considerably as a general-purpose household disinfectant, at least in France (44). Magnesium oxychloride has been suggested as a non-sparking floor covering when combined with a filler material; such a covering, it is claimed, would also prevent further oil seepage through an oil-affected floor and would make an oil-soaked floor burn less readily in case of fire (45).

Sodium chlorite and chlorine dioxide continue to be used widely in pulp bleaching and similar applications. Laporte Chemicals Ltd. have begun operations at the first U.K. chlorite plant (46). Sodium

chlorate now has its fastest growing market in pulp and paper bleaching but future growth may depend on its use as an oxidant in missile fuels (47). Ammonium perchlorate is also of increasing importance in solid propellant motors for rockets and missiles (48).

#### *Fluorine*

A triple-tank system, designed for transport of fluorine in 5000-lb. lots, comprises a tank for the liquid fluorine surrounded by a tank containing liquid nitrogen refrigerant and, outermost, one containing a granulated insulating material—silica gel—under vacuum (49). It has been suggested that fluorine, which is already used in rocket fuels, might be the rocket propellant of the future when used in conjunction with hydrogen (50).

#### *Hydrofluoric acid and fluorinating agents*

Hydrogen fluoride is yet another compound which is being produced in greater quantity. A group of engineers working for the U.K. Atomic Energy Authority has devised a rotary pump for operation in hydrogen fluoride. This has a long hollow shaft with bearings self-lubricated by an enclosed oil circuit, while a continuous flow of nitrogen from a low-pressure supply prevents hydrogen fluoride vapour from diffusing into the working parts and also ensures that oil vapour does not contaminate the liquid being pumped (51).

Sulphur tetrafluoride is now available commercially in limited quantities and is said to have unusual fluorinating properties for the simplified preparation of known fluorides and for interaction with a variety of organic carboxylic acids and carbonyl compounds (52). The use of stannous fluoride in toothpastes as an agent for preventing tooth decay has been approved in the U.S.A. (53).

#### *Bromine*

There has been some expansion of bromine capacity, notably in the U.S.A. and Israel, to satisfy the increased demand, which is due mainly to the need for ethylene dibromide, now used in large amounts in the manufacture of tetraethyl lead and in agriculture, especially on tobacco crops (54).

### **Peroxygen compounds**

#### *Hydrogen peroxide*

Several countries have increased their capacity and, at Warrington in Lancashire, Laporte Chemicals Ltd. are now operating what is believed to be the largest plant in the world, and certainly the first in this country, to employ the autoxidation of anthraquinones (55). The new plant has enabled the company to double

its output of high-strength hydrogen peroxide, which was used as the oxidant in the motor of the Black Knight ballistic missile (56). Degussa claim to have improved their autoxidation process by the use of a methyl-substituted aromatic ketone, such as *p*-(*t*-butyl)-acetophenone, as solvent for the 2-ethylantraquinone used (57).

#### *Salts of peroxy acids*

Potassium monopersulphate is now being used in household washing agents (58). Du Pont have patented a new industrial product—the triple salt of potassium sulphate, hydrogen sulphate and hydrogen monopersulphate,  $\text{KHSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{KHSO}_5$ , which can be used for bleaching various materials (58*b*) and is suitable for addition to household detergents.

#### **Nitrogen compounds**

During the last few years, production of nitrogen has exceeded consumption. In mid-1958, stocks in Europe were estimated at less than 300,000 tons—about 6% of production—and consisted mainly of ammonium nitrate and urea. In the U.S.A. and Canada stocks were more or less normal at that time. In order to keep stocks at reasonable levels and to prevent too great a drop in prices, producers in the U.S.A. worked at about 75% of their capacity and on the European Continent at about 80%. The biggest importer is mainland China. In Japan stocks are mounting and production is likely to suffer unless new markets are found, owing to the cancellation of part of the contract with China (59). According to the latest Aikman report (60), world production and consumption of nitrogen continued to increase but the excess of production over consumption is estimated to have decreased slightly during the last two years.

Chilean production during the year ended June 1959 was only slightly lower than in the previous year but non-mechanised producers had difficulty and were forced to cut production by about 10%. Most of these older producers are in serious trouble, because of the higher living costs, and some mines have been forced to cease production (59); however, credit has been granted by the U.S.A. to help modernisation plans, which should ease the position (61).

#### *Ammonia and ammonium salts*

There has been marked expansion in ammonia capacity in the U.S.A., particularly in the Western States, where there is already a glut of ammonia (62). Recently, Imperial Chemical Industries Ltd. began production at a 60,000 tons-a-year plant at Billingham, Co. Durham, for the production of ammonia from oil and at a 100,000 tons-a-year plant at their Severnside Works, with associated plants for urea and fertilisers (63). Details have been given



of a new U.S. ammonia synthesis process in which about 270 tons of ammonia are produced daily from refinery tail gas and air (64).

Ammonium sulphate remains well in the lead as a source of nitrogen in fertilisers (65). A new process for its manufacture has been developed in Spain (66) in which the sulphur dioxide content of smelter gases is absorbed in an organic base solvent and the sulphite oxidised to sulphate by injected air, the organic sulphate being then decomposed with ammonia and the product recovered by centrifuging and drying.

The main outlet for increased supplies of ammonium nitrate is for fertilisers but it has also been used as an industrial explosive (67). Fisons Ltd. have opened the first U.K. plant to use the du Pont process for oxidation of ammonia to nitric acid, followed by reaction of the acid with more ammonia to produce ammonium nitrate (68).

#### *Nitric acid*

Imperial Chemical Industries Ltd. have new nitric acid plants, one using the new I.O.P. (intermediate pressure ammonia oxidation) process, and two concentration plants using the magnesium nitrate route (69). In the I.O.P. process, ammonia is converted to oxides of nitrogen at atmospheric pressure and the gases, when passed to the absorption towers, are brought to 42 p.s.i.; the heat of reaction is used in the generation of steam for the process (70). In the concentration process, a 72% aqueous solution of magnesium nitrate is used instead of sulphuric acid, the nitric acid being concentrated from a strength of 60% to one of 99.5% acid (71), for use in the company's nitroglycerine plant.

#### *Other nitrogen compounds*

Anhydrous hydrazine, for use in rocket fuels, is now being produced for the U.S. Air Force by the Olin Mathieson Chemical Corp. (72). This product and unsymmetrical dimethylhydrazine are used in the fuel of the Titan II intercontinental ballistic missile, with nitrogen tetroxide as the oxidiser (73). In the U.S.A. there is also a project for fissio-chemical production of anhydrous hydrazine from ammonia directly, avoiding chlorination and other chemical reactions (74). A fully automatic plant has been installed at the Inoya Power Station in Hungary for the production of hydrazine for the treatment of boiler feed water (75).

Both nitrogen trifluoride and tetrafluorohydrazine, which show promise as oxidants in high-energy propellants for rocket motors, are being manufactured on the pilot plant scale by the Stauffer Chemical Co. (76). In the manufacture of tetrafluorohydrazine, nitrogen trifluoride is reacted with carbon in a fluidised bed and the product is separated from unreacted trifluoride and the by-

products—tetrafluoromethane and nitrogen oxides—by fractional distillation.

In addition to its well-known anaesthetic use, nitrous oxide has potential value in the U.K. as an aerosol propellant. It is already in use in food aerosols in the U.S.A. (77). Russian investigators have found that the addition of 0.5–1% of hydroxylamine sulphate to the electrolyte prolongs the life of lead-type accumulators (78).

### Phosphorus and its compounds

#### *Phosphorus*

Increased capacity and expansion of production for elemental phosphorus are reported (79). In the U.K., L. Light & Co. Ltd., after extensive research, have succeeded in producing both red and white phosphorus with a minimum purity of 99.999% (80).

#### *Phosphoric acid and phosphatic fertilisers*

An important feature in the field of phosphoric acid manufacture is the trend back to the use of the wet process; of seven new plants in the U.S.A. at least five employ the wet process (81). The Monsanto Chemical Co. plans to produce a phosphorus pentoxide-enriched 105% phosphoric acid called 'Phospholeum' (82), which is intended for use as a desiccant and as a sequestant for common trace metals, such as calcium, aluminium and magnesium. A new Japanese process for fertiliser-grade acid is believed to be a tower process in which raw phosphate is treated countercurrently with sulphuric acid, with unusually high-quality calcium sulphate as the by-product (83).

British exports of sodium phosphate, at 13,940 tons, were about 25% higher in 1959 than in the previous year (84). During the past eight years U.K. usage and exports of phosphatic fertilisers have shown a steady decline, while deliveries of nitrogenous and potassic fertilisers have tended to increase (85).

### Silicon and its compounds

Three new plants have been erected and another is in hand for the production in the U.K. of ultra-pure silicon for use in semi-conductors (86). A new material consisting of silicon nitride stiffened with a fine dispersion of silicon carbide has been developed by the Metallurgical Division of the Admiralty Materials Laboratory for use in stator blades in gas turbines at temperatures as high as 1200° (87). It is said to have excellent thermal shock and oxidation resistance and adequate creep strength at such temperatures. Silicon nitride is also potentially valuable for use in electrical insulators which are subject to violent temperature changes, e.g., on rocket launching platforms, and may also be of

use as a support for high-temperature catalysts, and for other purposes.

### **Boron and its compounds**

There is an increasing demand for boric acid, especially in the U.K. and European Common Market countries, and there are plans for expansion both in the U.K. and in France (88). In Italy, a new process has been developed to the pilot-plant scale (1000 kg./day) for the manufacture of boric acid from minerals of the colemanite type. The mineral is decomposed with a solution of ammonium bicarbonate containing free ammonia, followed by decantation or filtration, and the calcium carbonate and other insoluble matter present is removed. The ammonium borate solution is decomposed by boiling, with recovery of ammonia. The product is of high purity (89). Boric acid can be used in the preservation of wood, and a product giving the desired ratio of boric acid to borax in a single compound has been developed specially for this purpose (90).

The Dow Chemical Co. and the U.S. Borax Research Corp. are to engage in a joint venture for perfecting an economic process for manufacture of boron trichloride (91), which is a highly reactive intermediate from which many new boron compounds can be made.

### **Potash**

There has been some expansion of potash facilities, Eastern Germany being the world's largest producer. A new foundation has been established for International Potash Research by six major U.S. potash producers to develop programmes for the efficient and beneficial use of potash in various countries and, in particular, to work closely with agricultural authorities (92).

The International Minerals & Chemical Corp. (93) are now producing high-quality potassium chloride, in both coarse and standard grades, for use as a fertiliser. A flotation process was chosen for this because naturally occurring crystals are less subject to degradation than are granulated or agglomerated products during shipping and storage.

### **Calcium salts**

#### *Calcium cyanamide*

Süddeutsche Kalkstickstoff-Werke A.-G. have made considerable progress in calcium cyanamide manufacture. Based on the exothermic nitrogenation of calcium carbide in a horizontal rotary furnace, the process employs a finely powdered carbide feed of less than 0.2 mm. particle size; since this is a surface reaction, efficiency is inversely proportional to particle size and the process is claimed to be very favourable economically. In addition, some calcium

cyanamide is recycled to stop sintering and prevent the reverse reaction occurring. In another plant the rotating furnace used is combined with a preliminary fluidised-bed reaction step (94).

#### *Other calcium salts*

Among new calcium sulphate plants is one to recover from wet-process phosphoric acid manufacture by-product gypsum to be used for wallboard manufacture (95). A new, and rather unexpected, use for calcium chloride is in the manufacture of paperboard. It has been found that the addition of this salt to the pulp suspension, before its distribution on the wire of the board-making machine, assists in the removal of water (96). Large deposits of fluorspar are to be exploited in the Eastern Pyrenees; they are said to be among the largest in the world (97).

A new Dutch process for the granulation of calcium nitrate, formed as a by-product in the manufacture of nitro-phosphate fertiliser, has been described (98). The process is based on the crystallisation of droplets of calcium nitrate in mineral oil to which seed crystals have been added. After crystallisation, the solid prills are separated from the oil by centrifuging.

### **Miscellaneous**

#### *Zinc oxide*

A new process for the direct production of zinc oxide from sulphide ores by flash roasting has been described (99). The ore is dried to a moisture content below 0.5% and screened, and then fed into a specially developed furnace where the finer particles burn in suspension forming zinc oxide and fine slag, both remaining in suspension in the rapidly moving combustion gases; the temperature of combustion must be held within narrow limits. The product is said to be almost 99% pure and production costs are much lower than in conventional processes.

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## ROAD AND BUILDING MATERIALS

By MEMBERS OF THE ROAD AND BUILDING  
MATERIALS GROUP

CEMENT AND CONCRETE (P. E. Halstead, Ph.D., F.R.I.C.)

*Cement & Concrete Association, Wexham Springs,  
Stoke Poges, Bucks.*

### Cement manufacture

No outstanding advances have been made in the period under review but considerable interest is reported from the U.S.S.R. in non-traditional methods of cement manufacture. Krylov & Pomyan (1) describe the preparation of a Portland cement by fusion at 1900–2000° in an O<sub>2</sub>-enriched air blast and Ershov & Kashperovskaya (2) also describe work on fused cements of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system. The possibility of using fluidised-bed techniques in a shaft kiln has been examined with the aid of a model (3).

The effect of small additions of Cr<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub> and BaO has been investigated (4), and it is claimed that these oxides enter into and modify the alite solid solution structure, so improving the grindability of the clinker and the properties of the finished cement.

In a study of the relationship between the properties of cement and its granular composition Ivanov-Gorodov (5) mentions that gypsum requirements are more sensitive to small changes in grain size than in mineralogical composition.

A series of papers by Costa & Petermann (6) describe the use of radioactive tracers to study material transfer and dust evolution in rotary kilns and the causes of clinker ring formation have been reviewed (7).

### Special cements

The production and properties of hydrophobic Portland cements has attracted considerable attention and several patents covering the production of such cements have been granted, typically for the addition of such materials as oleic acid and waxes in amounts of the order of 1%. Hydrophobic cements generally are reviewed by Kosina (8). Schlünz (9) mentions the production of a hydrophobic gypsum-slag cement with improved keeping qualities.

Expansive cements based on calcium sulphoaluminates are described by Klein & Troxell (10) and the possibility of producing

intrinsically coloured cements by incorporating small proportions, typically 0.05–1%, of Cr, Mn, Fe, Co, Ni and Cu in the raw materials fed to the kiln has been examined (11).

Barium aluminate cements are described by Braniski (12) and are claimed to be superior in refractoriness to the corresponding calcium aluminate cements. A French patent (13) has been granted for a cement of this type.

### Cement hydration

Further electron microscope studies of hydrating cement are reported by Czernin (14) and Saji (15), and Schwiete *et al.* (16) have published a monograph on the hydration of  $C_3S$  and  $\beta$ - $C_2S$ .

Manabe & Kawaka (17) have described their use of  $^{36}S$  as a tracer in investigating the formation of calcium sulphoaluminates and the reaction between gypsum and calcium aluminate. The thermodynamics of the system  $CaO-SiO_2-H_2O$  at normal temperatures and under hydrothermal conditions have been examined in detail by Babushkin & Mchedlov-Petrosyan (18), who calculated and measured heats of hydration and of formation of the various compounds in the system.

A series of U.S.S.R. patents (19) describes claims relating to the reduction of heat evolution in the hydration of aluminous cements.

### Mortars and concrete

The carbonation of hydrated Portland cement products has aroused some interest. Cole & Kroone (20) have published an extensive review of the subject, while Blakey and Kroone (21) discuss the reaction of  $CO_2$  with mortars. Experiments on the artificial carbonation of masonry units and its effect on shrinkage have been described (22).

Curing conditions generally were the subject of a report by a committee of the American Concrete Institute (23).

Koch & Steinegger (24) have reviewed existing methods for assessment of the sulphate resistance of cements and propose a new rapid method based on the estimation of  $OH^-$  liberated by specimens immersed in  $Na_2SO_4$  solution.

Alkali-aggregate expansive reaction attracted little attention but Hansen observed (25) that there seemed to be a relation between the magnesia content of the cement and the amount of expansion when high-alkali cements gave an expansive reaction with some aggregates.

The factors affecting the corrosion of reinforcement in concrete have been investigated (26) and the effects of commercial additives have been examined (27). Shalen & Raphael (28) have continued their work in this field by studying the effect of using sea water for

mixing concrete and have described tests on mild steel in cement-water suspensions.

An interesting paper by Alexander (29) describes measurements of the strength of the aggregate-cement paste bond.

Epoxy resins have frequently been suggested for the repair of concrete and an example is quoted by Davis & Pinkstaff (30).

Sodium fluoride may be used as an admixture in place of calcium chloride, for winter concreting 2% sodium fluoride + 3% sodium chloride being equivalent to 15% calcium chloride + 5% sodium chloride (31).

### Analysis and testing

The principal innovation in this field has been the use of X-ray methods of analysis for raw feed and clinker. X-ray fluorescence may be used to determine Fe, Ca, Si, Al and Mg in raw materials (32) and an important series of papers from the Portland Cement Association (33) describe work on the estimation of the mineralogical composition of clinker by X ray diffraction.

The determination of chromium in cements (34) is of interest in connexion with reports (35) of dermatitis due to the presence of this element. The determination of fluorine in clinker is described by Bogdanova (36), and Francardi & Cremaschi (37) have discussed the interference by calcium in the determination of alkalis by flame photometry.

A hydrometer has been used for estimating cement content of fresh concrete (38). The ASTM method 186 for determination of heat of hydration was examined by Santarelli *et al.* (39) and a modification was proposed as an improvement. Hansen (40) and Sulikowski (41) have reported on false set, and the latter notes that false set increases the shrinkage of cement products.

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## CLAY AND CLAY PRODUCTS (W. Noble, B.Sc., F.I. Ceram., A.R.I.C.)

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### Mineralogy

METHODS of identifying many clay minerals have been simplified by recent sorption studies. After investigating more than 600 clays Keeling (1, 2) has found that corrected ignition loss/moisture adsorption ratios provide indices that are sensitive to changes in

composition and give characteristic values for a range of clay minerals. Evidence about accessibility to different mineral structures has been obtained from a study of absorption rates (3), and absorption by mixtures of clay minerals has been shown to be an additive function of the minerals present. The rate and amount of adsorption was also influenced by the exchangeable cation, the importance of which has been further stressed by Brooks (4) as a result of free energy considerations of adsorption isotherms. Good correlation between surface area and exchange capacity in mono-disperse fractions of a Florida kaolin has suggested (5) that the exchange behaviour of kaolinite was primarily a surface phenomenon but Holdridge (6) has indicated that limited isomorphous replacements of  $Al^{3+}$  by  $Fe^{3+}$  and  $Mg^{2+}$  may account for a considerable proportion of the cation exchange capacity of the kaolinite in ball-clays. Measurements of dielectric loss have been made on several clay minerals to detect lattice defects (7).

### Preparation and drying

Currie & Grimshaw (8) have confirmed equations that relate the viscosity of fully dispersed suspensions with concentration and have shown how thixotropic behaviour is enhanced by the presence of small particles and by excessive concentrations of electrolytes. The dominant effects, on the flow of plastic clay, of specific surface area and of ions or salts associated with the clay minerals have also been demonstrated.

Two recent papers dealing with extrusion (9, 10) have cited evidence of the orientation of clay crystallites at lamination and shear-planes. The theory of oriented and semi-rigid water layers on clay water systems has been applied and developed (11) to explain observations on the properties, drying characteristics and dry strength of products made by different methods over a wide range of moisture contents. Brooks (4) noted that adsorption results were influenced by re-drying, and Okuda (12) has found that rheological and some chemical properties of kaolinitic clays can be influenced by a previous 'drying history' through its effect on the bonding power or 'fixation' of adsorbed cations at the surface of the clay minerals. Indications of the strains developed during drying and of the tendency for inequalities in moisture distribution to persist in plastic clays have also been given (13).

### Firing

The range of application of the pyroplastic index (14) as a deformation characteristic of the clay during firing has been extended to cover products with different shape factors (15) and maximum values accepted in New Zealand for clay building products have been reported (16). Measurements of changes in elasticity at

different temperatures have been used (17) to explain an effect of grog additions on the control of cracking and deformation. Progress in the study of kiln design has been reported by Holmes (18).

### Properties and testing

Moisture expansion has now been recognised as an inherent property of clay wares and measures to limit and to accommodate the small changes in dimensions in buildings have been recommended (19), although the difficulty of designing tests to simulate conditions of usage is recognised (20). Norris and others (21) have differentiated between expansions associated with short- and long-term adsorptions, glasses and crystalline components and effects due to soluble salts.

The search for adequate tests for durability continues and measurements of size changes (22) and pore size distribution (23) have been made to help to elucidate factors favourable to frost resistance. An improved method for determining the sulphur oxides in flue gases has been described (24) and a British Standard issued (25) on the sampling and analysis of fuel gases.

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## GYPSUM AND ANHYDRITE, AND THEIR PRODUCTS

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A CONSIDERABLE number of papers have been published on the scientific and technological aspects of gypsum and anhydrite during the year under review, but it cannot be said that any considerable advance in our fundamental knowledge has resulted from them, nor have any of the out-standing problems been brought any nearer to being resolved. The dehydration products of gypsum have been studied by Razouk and others (1), by determining their sorption isotherms with water vapour. It is suggested that insoluble anhydrite, when exposed to what is called saturation vapour pressure, may first hydrate to hemihydrate. The controversy over the existence of two forms of hemihydrate— $\alpha$  and  $\beta$ —continues. Powell (2) has shown that the rates of formation of soluble anhydrite from hemihydrates prepared in two different ways, one said to give the  $\alpha$ -form, the other the  $\beta$ -form, were very similar, but the rates at which insoluble anhydrite formed were quite different, being much greater for the  $\alpha$ -form. This difference has been confirmed by Mitsuki & Kita (3), who, however, show that the rate can vary with the physical condition of the sample and with the rate of heating. Powell (4) has now used this phenomenon to demonstrate that hemihydrate, commercially produced in a kettle, consists of  $\alpha$ - and  $\beta$ -forms and does not contain, as has been suggested by Eipeltauer (5), forms intermediate in properties between the two.

The hydration process of hemihydrate has been studied by Ridge & Hill (6) with particular reference to its variability from one commercial plaster to another. They conclude that the variation resides chiefly in differences in the density of seeding nuclei and suggest that most of the nuclei in plasters are due to potential nucleus-forming sites on the surface of the hemihydrate rather than to discrete grains of gypsum. A proportion of these nuclei are readily destroyed by re-heating the plaster, and the density of the residual nuclei differs greatly between plasters. They suggest that the density of residual nuclei may be related to the density of dislocations in the hemihydrate crystals which, in turn, depends on the previous history of the plaster and the type of impurity present.

The considerable work carried out by the C.S.I.R.O. Australia on the properties of set hemihydrate plasters containing perlite, with particular reference to their dimensional stability, has been set out in a report (7). It is concluded that the expansion of perlited plasters subsequent to setting is caused by the rehydration of the

perlite but that, in general, the forces involved should not lead to trouble in practice.

The difficulty sometimes found in obtaining an adequate bond between set gypsum plaster and concrete made with certain types of aggregate has been dealt with in some detail by Ryder (8). It derives from the lowering of the coefficient of thermal expansion of concrete when aggregates such as limestone or crushed brick are used. This lowering increases the differential thermal movement between set plaster and concrete and most of the failures followed a rise in temperature of the structure.

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## LIME AND LIME PRODUCTS (G. E. Bessey, M.Sc., F.R.I.C.)

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### Lime

THE development of the lime kiln from early times to the present day has been reviewed by Azbe (1), with particular emphasis on the current trends in gas-fired kilns in the United States, where the increasing use of natural gas has favoured the improvement of such kilns (2). Mixed-feed kilns have been more thoroughly investigated in Europe. Three papers by Eigen (3) continue the author's intensive study of kiln parameters and reactions in the coke-fired vertical kiln. Practical problems in applying theoretical knowledge to actual kilns of this type have been discussed by Hoffman (4), and a set of nomograms for operating mixed-feed kilns under various working conditions has been developed (5). The rate of decarbonation of calcium carbonate and the properties of the resulting quicklime have been studied as a function of shape and

size of the limestone lumps, and of the burning conditions (6), including fluidised operation (7); similar studies were made for dolomite (8). For making sulphur-free lime it has been proposed (9) to use basic coke, made by adding lime or calcium carbonate to the coal from which the coke is made, the sulphur being retained by the ash of such coke. The mechanism of the corrosion of kiln linings has been further studied (10).

Methods for improving the quality of hydrated lime, particularly its plasticity, continue to be devised. Thus the temperature of hydration, which is probably the primary factor, may be varied automatically according to the particle size of the quicklime feed (11) or, in making a lime putty, the proportion of water and quicklime may be varied in accordance with the continuously determined consistency of the product (12). A novel method of producing hydrated lime has been patented (13), in which hydrated lime is produced from raw limestone in a single continuous plant where both burning and hydration are carried out in the fluidised state. The hydration of softly burned lime (900°) was the subject of a detailed study by Pleva (14), who showed that the lean putty usually obtained on hydration can be much improved by preliminary partial hydration of the quicklime in a damp atmosphere, preferably followed by ball-milling of the fully hydrated product or treatment in an 'activator' (essentially a high-speed mixer). The effect of adding alcohol, formaldehyde, and surface-active substances during hydration can also be beneficial, and an explanation for these effects is offered. Glasson (15), continuing his studies of the mechanism of the reaction of calcium oxide, has measured the rates of hydration under various conditions.

The possibility of using hydrator residues for making cement (16) and, with addition of clay, for lightweight concrete units (17), has been investigated. Heating quicklime with clay at the comparatively low temperature of 450-750° yields an artificial hydraulic lime (18). Minerals formed in lime-clay reactions and in the hydration of their products have been identified (19).

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### Sandlime bricks and other silicate products

The hydrothermal hardening reaction which takes place in the manufacture of these products has been further investigated (1) and the nature of the hydrated silicate bonding material continues to be studied (2). Definite mineral compounds which have been identified include tobermorite, xonotlite and nekoite.

Large perforated blocks are commonly used on the Continent, and some very large units, not always perforated, are being made in the U.S.S.R. (3). Aerated sandlime products, which have been known for some time, particularly in Scandinavia, are receiving more attention (4). Lightweight-aggregate products have also been made (5).

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**ROAD MATERIALS (K. E. Clare, B.Sc., A.R.I.C.)**

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**Soil stabilisation**

PARTICULAR attention has been devoted this year to matters of interest to chemists connected with roads in the Commonwealth. In the study of road foundations the character of the clay in the soil is being recognised as of importance. Since the tropical weathering of rocks is especially intense it is not surprising that the variety of clay types present in tropical soils is found to be wider than with soils in temperate climates. Grim (1) has reviewed recent knowledge of the structure, composition and origin of clay minerals, and the ways of identifying them. Lambe & Martin (2) have compared the mineralogical composition and engineering properties of 33 soils, including some from the tropical belt. An investigation in Ghana of soil stabilisation with cement (3) has shown that the majority of 75 soils investigated can be stabilised satisfactorily by the addition of 3–7% of cement. Ghana is divided into three soil regions, each having a typical relation between unconfined compressive strength and cement content which is believed to be influenced by the composition of the soil, which in turn may be determined by vegetation cover. Cement-stabilised laterite gravel has been used in the construction of a large new runway at Darwin airfield in Australia (4), and the use of similar material in the Rhodesias has been described by Keeble (5). The successful use of hydrated lime for the stabilisation of soils in Northern Rhodesia has been described by Cartmell & Bergh (6), while Campbell has described the use of the same stabiliser in Kenya (7).

Among methods of soil stabilisation used in French overseas territories, Peltier (8) has described the use of bitumen and of amines or quaternary ammonium salts which make soil hydrophobic. Slow-breaking bitumen emulsion has been used (9) for the stabilisation of crushed shell and sand in airfield runway con-

struction in Senegal. Uppal (10) has described Indian experiments in which five types of bitumen binders were used to stabilise sandy loam soil. Additive contents of 4% gave satisfactory results. Kolyasev & Holodov (11) have described the waterproofing of soil by wood tar, naphtha soap and dimethyloxysilane. In India, cohesive soils were waterproofed in the laboratory by the addition of linseed oil cake (12). The surface of sand embankments can be stabilised by spraying with sodium silicate solution followed by a solution of calcium chloride (13).

### Weathering of road surfaces

Some of the factors which influence the weathering of road pavements are more active in tropical than in temperate climates. Gallaway (14) has related the durability to chemical composition and rheological properties for bitumens used in surface dressing at 11 sites in Texas, where the climate is similar to that in certain parts of Africa. In the Union of South Africa, a method has been developed for measuring the viscosity of very small samples of bituminous binders for studies of weathering on the road (15). Kleinschmidt & Snoke (16) have studied in the laboratory the effect of light and water on the degradation of bitumen. Tingle & Wright (17) have examined the important effect of oxidation in the weathering of road tar incorporated in open-textured surfacings.

The National Institute for Road Research in South Africa (18) report a full-scale experiment designed to compare the performance of various types and quantities of bitumen in pre-mixed bituminous carpets. Tentative recommendations for the specification of premix composition are made, based on the results obtained. Bryan (19) has advocated the use of sand-bitumen surfacing for a main road in British Guiana. Dead reef oyster shell, found in the coastal area of the Gulf of Mexico, may be used as an aggregate in hot- and cold-mix bituminous surfacings (20). Malik (21) has described research into the use of shell-rock found in Southern U.S.S.R. in bituminous road construction. Dickinson (22), reporting experimental work in South Africa, notes that the addition of 3% or more of rubber to the bitumen improves the resistance to reflection cracking of the slurry seals that are now finding increasing use for the maintenance of cracked bituminous surfacings.

### Use of concrete

The chief use for concrete on highways in the tropics is in bridge construction. Many of the gravel aggregates available are porous. An investigation has been made on the effect of water absorption by aggregates on the water/cement ratio of concrete (23). Klieger (24) has studied the effect of the temperature during mixing and curing on the strength of concrete made with Portland cement.



Newman has experimented with mixes containing a high alumina cement (25) and his results enable an estimate to be made of the eventual strengths of concrete cured for long periods under hot and moist conditions. High humidities in some parts of the tropics can lead to deterioration of cement in storage. Stoll (26) has described laboratory tests showing the greater resistance to moisture during storage of 'hydrophobic' cement containing small amounts of oleic acid.

### Use of resins and plastics

The uses of adhesives with an epoxy resin base for repair of footways, gutters and carriageway surfacings, the bonding of extruded concrete kerbs to the road surface, and the provision of traffic markings have been reviewed (27). Other uses include the anchoring of runway pavement dowels and the repair of spalled pier-caps on a concrete bridge (28). Vinyl and polyethylene films have been investigated as means of protecting road foundations from changes in moisture content (29). A laboratory test for the resistance of the films to puncture is described; the vinyl film was found to be better than that of polyethylene.

### Herbicides

Chemicals used for the control of vegetation at roadsides include sodium chlorate, selective weed killers of the 2,4-dichlorophenoxy-acetic acid type and grass growth inhibitors like maleic hydrazide (30). The technical and economic aspects of chemical roadside verge maintenance in the United Kingdom have been reviewed (31). A recent development has been the introduction of 2-chloro-4,6-bisethylamino-s-triazine as a comparatively non-selective herbicide (32). Duthie (33) has summarised the papers and discussion of the First East-African Herbicide Conference, and the Colonial Pesticides Research Unit has listed the proprietary herbicides available in East Africa (34).

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## GLASS

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OVER the period under review steady progress has continued in most fields of glass technology, and it is difficult to give a complete picture of all the progress that has been made. A selection of the main items has therefore been made, leaving other fields to be covered by the references in the supplementary bibliography.

A number of points of general interest should first be mentioned. The Fifth International Congress on Glass was held at Munich in June-July 1959. The new research laboratories for Pilkington Brothers at Lathom Park, near Ormskirk, are now nearing completion and when in full operation are expected to be the largest glass research laboratories in the world. After a life of 45 years, the *Journal of the Society of Glass Technology* ceased publication at the end of 1959 and was replaced by two separate publications, (a) *Physics and Chemistry of Glasses*, dealing with the more theoretical aspects of the vitreous state, and (b) *Glass Technology*, which will concern itself more with the applied and technical side of glass making. It is hoped that by this it will be possible to publish more papers of a specialised nature than in the former single journal.

### Glass compositions

In the main fields of glass manufacture, the majority of glass compositions used remain virtually unchanged for decades, but for special applications, glasses with abnormal properties may be required, and investigations into glass-forming systems are therefore continuously in progress. For example, King and his associates (1, 2) have investigated the infra-red transmitting properties of antimony oxide glasses. The system  $R_2O-Al_2O_3-Sb_2O_3$  transmitted wavelengths up to  $6.2\ \mu$ , while some glasses in the system  $K_2O-Sb_2O_3-Sb_2S_3$  transmitted up to about  $8\ \mu$ .

Glasses of high refractive index and dispersion have been produced with the  $Na_2O-TiO_2-SiO_2$  system (3), while the search for heat-resisting glasses prompted the investigation of the zinc borosilicate system (4). Extra-dense glasses as protection against atomic radiation are usually produced from lead silicate glasses, but recent work on the  $Bi_2O_3-PbO-SiO_2$  system has yielded glass with

densities of nearly 8 g./cm.<sup>3</sup> (5). A series of four papers (6) deals extensively with binary phosphate systems; density, surface tension and infra-red spectral measurements are made and the results are discussed theoretically.

Recent work at the Bell Telephone Laboratories (7) has produced some glasses with low melting point which are highly fluid below 400°. These glasses belong to the ternary systems As-S-Tl, As-Se-Tl and As-S-Se. Because of their low melting points, they have obvious applications in the hermetically sealing of electronic and other devices, by a simple dipping process. The use of iodine and bromine in place of thallium has resulted in the production of glasses fluid at room temperatures (8).

### Glass melting

The Symposium on Glass Melting (Brussels 1958) (9) produced a considerable number of papers dealing with the physical and chemical aspects of the melting process.

The effect of the grain sizes of raw materials on the rate of melting and refining had been the subject of much investigation (Cable; Jaupain & Brichard, 9). The conclusions suggest that a quicker melting rate can, in general, be achieved by the use of finely ground materials, but this gain can easily be nullified by the longer refining time required. The effects of briquetting and moistening the batch were also shown to reduce melting time (Eloy, Jaupain & Plumet 9; see also 10).

The use of special materials to assist in the melting and refining of glass is normal glass-melting practice but the mechanisms by which these operate are still not fully understood. The use of arsenic oxide and sodium peroxide is described by Cable (9) and a number of papers (9, 11) are devoted to the use of sulphate. The results of such investigations are those of Baak (12) on the thermodynamics of arsenic in glass are obviously of prime importance in deciding the actions of refining agents.

Differential thermal analysis as a tool for the study of batch reactions was described in three papers at the Symposium (9). On more theoretical lines the glass melting process is discussed in relation to glass structure (13).

### Furnaces and refractories

One important aspect of furnace design is the reduction of heat losses to a minimum. A complete study of the losses from a furnace shows that there are many avenues which could lead to improved efficiency, and this type of study has been pursued by Bosnjakovic (14), and Huhmann-Kotz (15) using an 'exergy' as opposed to an energy balance. The 'exergy' is a quantity signifying 'work availability' and is related in a simple way to enthalpy, entropy

and temperature. The use of this quantity has certain advantages in that it stresses (i) the large change in entropy which occurs on combustion, and (ii) the small use that can be made of large amounts of energy at low temperatures.

Energy losses from the furnace structure can be dealt with most obviously by the use of insulating material. The main objection to this is the possible increase in temperature and hence corrosion of the hot face of the refractory blocks in contact with the glass. Kruszewski (16) describes trials, however, in which electrocast sidewall blocks were insulated without any apparent increase in wear. This appears to be confirmed by experiments on air cooling of tank blocks (17), which show that this has little influence on the glass refractory interface temperature while the blocks are of a reasonable thickness.

Heat recovery by means of recuperators and regenerators brings many problems and there is now a considerable preference for the use of basic refractories for regenerator packing material. Basic bricks of the magnesite type have a high thermal conductivity and bulk density and might be expected to be more efficient than fireclay, but as the thermal diffusivities are very similar, the only thermal advantage of the former seems to lie in its greater heat storage capacity (18). Another advantage of a basic material is its resistance to alkalis and lead oxide, but it is readily attacked by boron compounds.

The study of the attack of refractories by glass is constantly being pursued, and Ford (19) discusses how phase equilibrium diagrams can yield information on the corrosion of acid refractories. Electrocast refractories are less uniform in texture than normal fireclay material and the effect of this on the rate of corrosion has been studied (20). There is a definite correlation between crystal size and rate of solution, the glassy phase being attacked more readily than the crystals. Busby (21) has studied the attack of batch materials such as potassium carbonate, sodium sulphate and lead oxide on superstructure and regenerator refractories, and shows that the influence of porosity is important.

### Wetting of platinum

Because of its ability to withstand long periods of exposure to molten glass without any protective coating, platinum (and its alloys) finds considerable use as a refractory material, and a number of papers are devoted to the investigation of the wetting of platinum by molten glass. In the use of platinum as a crucible material, or as a bushing for the production of continuous filament fibre-glass, it is advantageous for the glass not to wet the metal. The last of a number of papers by Pask *et al.* (22), deals with the wettability of gold and platinum by sodium disilicate. The contact

angle for platinum was found to be very sensitive to atmospheric conditions; at 1000° the angle was 60° *in vacuo* or in helium, decreasing to 43° in hydrogen, while in air or oxygen complete wetting occurred. Dietzel & Coenen (23) have established a relationship between the wettability of Pt-Rh, Pt-Au and Pt-Be alloys and the reversibility of their electrochemical properties. The diffusion of oxygen atoms from the glass in the metal is believed to be the cause. Some Russian work (24) in connexion with glass-fibre bushings showed that more easily oxidised metals or alloys are more easily wetted.

### Flow of glass in tank furnaces

A knowledge of the flow of glass in tank furnaces is of great importance both to the furnace designer and to the glassmaker. The investigation of currents and flows in an actual furnace presents some difficulty. The usual procedure is to add some easily detectable material to the batch and measure its concentration in the glass leaving the tank. Lehoucq (25) used cerium oxide, which can be detected by its effect on the ultra-violet transmission of the glass at a wavelength of 325  $\mu$ . Radioactive isotopes were used by Moody & Monk (26), but there were difficulties of shielding and handling. These were overcome by Barker (27), who added small amounts of tantalum pentoxide to the batch, and the concentration of this in the final glass was detected by irradiating the samples and measuring the induced radioactivity of the tantalum. These methods give little indication of actual currents in the furnaces, and are used mainly to determine flow rates.

The currents are studied by the use of models at room temperatures. Dimensional analysis must be used to establish the similarity criteria, and it has been shown (28) that full dynamic similarity is theoretically unattainable. However, by making certain simplifying assumptions it is possible to arrive at criteria which can be achieved in practice (29-31). A number of papers (29, 32-34) describe experimental work with models, which can represent either the whole furnace or only a part of particular interest such as the model of the bridge-wall and throat described by Naruse (32).

In a theoretical paper Michaels (35) concludes that a tank furnace is not an efficient mixing device and cannot make good the results of bad batch mixing. He gives a general theory of tracer experiments and an extensive bibliography. Cooper (36) also discusses the subject theoretically and compares the theoretical results with those obtained in practice.

### Chemical analysis

A symposium on rapid methods of analysis was held by the Society of Glass Technology in November 1958, and the papers

given are fully reported (37). The methods discussed include the use of EDTA, which forms stable complex compounds with almost all metals. Three papers were devoted to the uses of the flame photometer, which is becoming increasingly popular for the determination of sodium, potassium and lithium in glass.

Spectrographic methods also have the advantage of speed and it is claimed (38) that an automatic recording spectrograph can carry out an analysis in under 5 min., which is considerably shorter than the 30 min. required for the preparation of the specimen. It is usual to determine the alkalis (by the flame photometer) and silica separately, so that a complete analysis without the silica can be performed in about 3 h.

Pyrohydrolysis techniques for the separation of fluorides have been known for some time, and these are now being applied to the analysis of fluorine in glass (39). Superheated steam is passed over the sample mixed with a catalyst ( $U_3O_8$ ) and the distillate titrated for fluoride. A similar technique is also being used for the determination of boric oxide in glass (40).

The analysis of boron by neutron absorption activation has again been mentioned (41) and an accuracy of about 1% is claimed. The method is rapid, taking about 10 min., but a large sample is necessary.

### Defects in glasses

The identification of the various solid inclusions likely to occur in glass is often a difficult problem. de Marchi & Romagnoli (42) discuss the processes which can give rise to stone and gall. Particular attention is paid to siliceous and aluminous inclusions, and very fine, useful photographs are given. Inclusions originating from zirconia refractories have been investigated by Jebsen-Marwedel (43).

Glassy inhomogeneities or cords are the subject of a number of papers at the 19th Conference on Glass Problems (44). Gehring & Francel discuss the types, causes and identification of cords, while other authors concentrate more on their control and elimination by such means as mechanical and electro-thermal stirring. Agitation by bubbling is cheap to instal and very effective. Löffler (45) has devised a method for distinguishing between batch and refractory cord based on the sudden composition changes which usually occur when refractory cords are present. Fluorescence under ultra-violet light can be used to identify some surface cords, especially those containing zirconia (46).

The commonest and most obvious defect in glass is the occurrence of bubbles, and the problem of gases in glass both as bubbles and in solution is constantly being studied. Greene and his associates (47, 48) have studied the rate of absorption of oxygen bubbles

in glass, and have found the diameter to decrease linearly with the square root of the time. Methods for the sampling and analysis of bubbles are mentioned (49, 50). A condensed translation of a Russian book by V. T. Slaviyanski in 'Gases in Glass' (51) discusses the interaction between gases and glass, the formation and analysis of blisters and the extraction and analysis of absorbed gases. The extracted gases can be analysed by first cooling in liquid oxygen, which will condense a number of gases (52). The presence and quantity of these gases can then be measured by investigating the vapour pressure as the temperature of the condensate rises.

### Miscellaneous

A modified process is now being used to make glass fibres. It is the 'Crown' process in which the glass from the tank runs into revolving spinners and is flung out through the fine holes which they contain. The product obtained is said to be of a more uniform and fine consistency and gives more efficient insulation.

An unusual use for glass which is receiving some attention is its use as a source of supply of trace elements in plant nutrition (53). The glass is used in a finely powdered form and can be used to supply Cu, Fe, Mn, B, Mo and Mn. Tests on orange seedlings showed that an initial application of 125 lb./acre was adequate to maintain growth for at least 10 months.

Since the discovery of methods of production of ceramic materials from glass (such as Pyroceram), discussed in the Report for 1958, more details of the properties of these materials have become available (54). Glass-ceramics are approximately 40% harder than borosilicate glass as measured by indentation tests, but they can be ground by normal methods while in their glassy state and precision grinding can be carried out in the crystalline state. Although the properties vary somewhat from type to type the softening point is about 1250° with a modulus of rupture of around 20,000 p.s.i. Lillie (55) gives a historical summary of the work of Stookey and others in developing photosensitive glasses and glass-ceramics. Stookey's paper (56) discusses the principles of nucleation and crystallisation in glasses and goes on to give brief descriptions of the process of making glass-ceramics with specific examples.

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## CERAMICS AND REFRACTORIES

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### General trends

RESEARCH and development in ceramics continues to favour well-defined, chemically pure systems to which fundamental concepts can be applied. In consequence it is less and less necessary to marry research programmes to particular divisions of the ceramic industries.

The increasing possibility of applying new knowledge of the solid state, particularly in its structural aspects, and of chemical kinetics to unresolved problems in refractories and ceramic technology has been indicated by Green (1). The ceramic technologist can only understand industrial processes by appreciating the inherent characteristics of the materials processed, which, being solids, are largely those of defect lattices (see later). The most important process is that of sintering (2).

The preface and content of the latest work from Kingery (3) makes the same point. 'The basis of the book can be expressed in the idea that ceramics are better considered as a *class of materials* than the product of a special industry.' He goes on to plead that even this is but a temporary view. A science of materials in general, including metals, plastics, ceramics, etc., must first be studied, with specialisation in ceramics to follow. If this is true, then new entrants and the outlook of industrialists must match, forcibly put by one of the latter (4). In 1959 the Basic Science Group became the fourth full Section of the British Ceramic Society.

A feature of the last two years has been the output of books concerned with ceramics (5). As this includes a knowledge of the solid state - another active field - it is a matter of personal judgment where to draw the line (6). There have also been books concerned with high-temperature materials and techniques (7), refractories (8), clays (9) and a commemorative volume (10). A new annual review has appeared (11) and also a work on ferrites (12).

As measured by papers and patents, the largest volume of research and development has been in the fields of special ceramics and ceramic-metal combinations. In this context ceramics are often non-oxide bodies, such as carbides and nitrides. Whereas

formerly ceramic-metal combinations generally implied sintered mixtures of finely powdered ceramic and metal, it now has to cover other types of geometry. These include metal grids filled with ceramic for nose-cones (7c), metallised ceramics and flame-sprayed metals or even the latest type of steel-furnace roof brick—the 'double E' brick—which is subdivided inside by sheets of metal to separate the magnesite-chrome refractory into columns to confer greater resistance to wear.

### Cermets

Cermets are making slow progress in application. The Haynes Stellite Co. of U.S.A. noted for titanium carbide cermets—offer parts up to 42 in. long. Tubes can be threaded for jointing, while blocks, tiles and other shapes are available (13). Some applications to chemical industry in the U.S.S.R. have been described (14). Larger and more complex shapes can be made in principle by flame-spraying on to expendable formers (7c). Uses under reducing conditions include submerged liquid-metal pumps for sodium-potassium alloys for use up to 1050°. This suggests that assessment in terms of oxidation resistance is not necessarily valid.

The interaction between graphite and a number of metals at about 1000° has shown copper to be least reactive (15). A novel method of making cermets is by the thermite reaction (16). Silicates such as zircon form silicides ( $ZrSi_2$ ) and borates form borides, e.g.  $TiB_2$  from  $TiO_2$  and  $B_2O_3$ . The method ensures high temperatures and no special atmosphere is necessary, but it is lacking in control, whilst the properties of the materials are inferior to regular cermets made by powder metallurgy methods.

### Clays and ceramic bodies

Brindley & Nakahira's brief note in 1958 on mullite has been expanded into an important contribution to our knowledge of the action of heat on clays (17). Some rarely available single crystals of kaolinite, 0.1 mm. in size, made it possible to study the orientation of the reaction products with respect to the kaolinite crystal axes. The observation of Comeforo *et al.* (18) that mullite needles formed parallel to the hexagon edges of kaolinite was confirmed. The erstwhile  $\gamma$ -alumina has been recognised as a spinel containing both aluminium and silicon atoms with many vacant sites. Mullite forms from the spinel phase. A structure for the amorphous 'metakaolin' first formed by the loss of the elements of water has been proposed. It is emphasised throughout the work that there are small and progressive changes of structure as heating proceeds. The atoms, as it were, are 'lazy' and inclined to move no more than is necessary to achieve reasonable stability. This is an example of 'topotaxy', a word used by Lotgering. This

view seems to be accepted on different evidence by Budnikov & Mehedlov-Petrozian (19), who show that sillimanite ( $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ ) and mullite ( $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ) are about equally likely to be formed from clay on thermodynamic grounds (within the limitations of the thermal data), but kinetic considerations are paramount.

From Brindley's laboratory also comes quantitative X-ray work on simulated pottery bodies, made up from kaolinite, mica and quartz in several proportions (20), and fired for 2 h. at  $1300^\circ$ . In general the crystalline phases correspond in amount with expectation on the basis of the  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  phase diagram, particularly as regards the mullite, but cristobalite tends to be underestimated, perhaps because of the distortion in the lattice found by Flörke. At  $1100^\circ$  and  $1200^\circ$  equilibrium is not reached in 2 h.

The kinetics of the glass-making process in which sodium and calcium ions enter the silicate network has been discussed by McKinnis & Sutton (21), mainly on the basis of the quantitative X-ray work of Abou-El-Azm & Moore (22). They give reasons for supposing that when melting occurs at no more than 100–250° above the liquidus temperature, a silica structure characteristic of the primary crystalline phase persists in the glass. At higher temperatures a degradation and reorganisation of the silicate structure occurs. There is a possibility therefore of reconciling the Warren random-network theory of glass structure and the micro-crystallite theory, favoured in Russia and elsewhere.

### Rate processes in solids

When dissimilar solids are brought in contact reaction is liable to occur, particularly if the temperature is not too far below the melting point of each. Examples of this occur in furnaces where magnesia reacts with silica or fireclay at about  $1500^\circ$  to form melt. This can be explained in terms of the formation of a lower-melting eutectic, which flows away to permit further reaction. A more intimate analysis can be made of this type of reaction along the lines referred to above (21). It is seen to be one case of diffusion where the product is liquid.

When the product is solid, an intermediate layer will form; thus, when magnesia reacts with silica, forsterite ( $\text{Mg}_2\text{SiO}_4$ ) is formed at, say,  $1900^\circ$ . The proportions of the solids in contact are less important than the crystal geometry and speed of diffusion of the participating ions. It had been shown by Kirkendall (23) that zinc diffuses out of brass more rapidly than copper diffuses in. In further experiments (24) inert markers at the interfaces of the copper-brass-copper sandwich moved towards each other at a rate proportional to the square root of the time, indicating that the marker movements were closely related to the diffusion process

itself. (For simple random-walk diffusion, the mean square displacement of the particles is given by  $x^2 = 2Dt$ , so  $x$  is proportional to  $t^{1/2}$ ).

To explain these results the idea that atoms reside at *all* the lattice points is given up in favour of an imperfect lattice, that is, one in which a few atoms are missing or displaced. The number of vacant lattice sites is a function of the energy needed to produce the vacancy and the temperature; the higher the temperature the greater the proportion of vacancies. Atoms diffuse by jumping from one vacant site to another: in the process the vacancies move the other way.

In the experiments with brass referred to above, the markers are assumed to remain fixed with respect to the lattice. Barnes (25) repeated these experiments and showed that there was an overall volume increase of the compact, seen to be associated with voids. The density decreased at a rate proportional to the square root of the time of heat treatment. In this Report for 1956 reference was made to Rigby (26), who drew an analogy between the behaviour of the zinc-copper couple and the phenomenon of bursting of chrome-magnesite bricks in the roofs of steel furnaces, where the atmosphere is rich in iron oxide. He showed experimentally that the magnetite diffused faster than ferrous chromite. It is generally assumed that the voids originated from the discharge of vacancies at grain boundaries, but for a complete discussion it would be necessary to consider the movement of dislocations.

In ionic solids the removal of an ion leaves a charge of opposite sign in the vicinity which must be balanced by the removal of an ion of opposite sign to the first to preserve electrical neutrality (Schottky defect). The number of Schottky defects in an ionic solid can be increased much above the normal equilibrium proportion by substitution, e.g.  $\text{Ca}^{2+}$  for  $2\text{Na}^+$  giving one vacancy for every substitution. Again, when alumina dissolves in magnesium aluminate ( $\text{MgAl}_2\text{O}_4$ ), it can be looked upon as a case of replacing  $3\text{Mg}^{2+}$  by  $2\text{Al}^{3+}$ , giving one vacancy per substitution. If this continues to the limit, the end product is  $\gamma$ -alumina with one-ninth of the sites vacant. Another example is wüstite, which can be regarded as a solid solution of  $\text{Fe}_3\text{O}_4$  in  $\text{FeO}$ , where two  $\text{Fe}^{3+}$  and a vacancy replaces three  $\text{Fe}^{2+}$  ions. An element forming two oxides often forms non-stoichiometric compounds, whereas there is less tendency where only one oxide is commonly known, as in  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , etc.

For some time there was doubt as to whether a hydrogen atmosphere influenced the sintering of alumina. It has now been shown that between 1500° and 2000° alumina sinters faster in dry hydrogen than in oxygen, helium or wet hydrogen (27). The apparent energy of activation of the process is very high at 230 and 135 kcal. per mole for dry hydrogen and the other gases



respectively. It is thought that these may correspond to control by diffusion of oxygen ions in the first case and aluminium ions in the second (28). Coble found 165 kcal. per mole for sintering of alumina in oxygen in fair agreement (29). Similar very high values are being reported but the diffusing species cannot be identified with certainty.

The mode of preparation of the powder prior to sintering is important. Van der Waals' forces may help to form an initial bond between glass particles (30). Beryllia calcined at 1250° gave lower fully sintered density than when pre-calcined at 1300 to 1400 (31). Quirk has discussed the impact of temperature of calcination on final density of beryllia and, incidentally, found an apparent energy of activation of 249 kcal. per mole for sintering (32).

The rôle of impurities is known to be important, but is not yet fully understood. Accidental impurities in the furnace atmosphere may produce a film of flux and give a viscous flow mechanism where a bulk diffusion process would be expected (28). Accidental impurities in the starting materials may have accounted for varying rates of sintering of zinc oxide (33). Deliberate additions must only be made to very pure starting materials if meaningful results are wanted. In one case (34) only  $\text{Cr}_2\text{O}_3$  amongst many additions lowered the rate of sintering, apparently from the formation of spinel with the primary magnesia.

Current views on sintering mechanisms have been rather fully exposed during the past two years at the Endicott House, Massachusetts symposium (5c), in London (30) and at Amsterdam in 1960 (to be published). One of the most interesting new aspects for chemists is the realisation of the rôle of gas atmosphere. Where there is an element in common, this will exchange at a measurable rate. Several lines of work in this field reinforce this conclusion, but direct evidence from oxygen-18 tracer work on calcium zirconate is available in the work of Kingery (35).

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## EXTRACTION AND REFINING OF METALS

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### Mineral dressing

THE study of the mechanism and kinetics of flotation processes continues to attract the bulk of the research work in this field; some work has, however, also been reported on methods of electrostatic and electromagnetic separation of minerals.

At the International Mineral Processing Congress held in London in 1960 Plaksin (1) reported that micro-autoradiographic and electronographic methods and potential measurements enabled the distribution of reagents on mineral surfaces to be determined both qualitatively and quantitatively as well as the stability of fixation and mobility of the reagent layers in relation to components of the gas phase. The crystal structure of the mineral influences the action of gases and the interaction with reagent. More effective separation of many minerals is possible by utilising the action of oxygen, nitrogen, oxidising reagents and others on the surface of the mineral particles.

A kinetic investigation of the effect of contact time, temperature and surface conditions on the adhesion of bubbles to mineral surfaces (2) has shown that there is a linear relationship between the logarithm of the minimum contact time and the reciprocal of the temperature, the slope of the line depending on the concentration of the collector and being zero at high concentrations. A thermodynamical treatment of the attachment of air bubbles to flat solids (3) indicates that about half the interfacial energy available in the system is expended in deforming the air-liquid interface in the absence of gravitational and kinetic energies; contact angle is a measure of this deformation during attachment. The deformation depends on the shape of the solid and on gravitational and kinetic effects, consequently contact angles determined by experiments with fairly large bubbles or drops cannot be used in Young's equation without introducing a correction for gravitational effects; this correction becomes particularly significant when the angle is small, i.e. at the threshold hydrophobic character of solids.

Other Russian work reported at the Congress dealt with the kinetics of flotation reagent sorption (4) and the physical stability

of collector adsorption layers on mineral surfaces (5). When sorption is insufficient to produce a monolayer the rate of sorption is generally proportional to the reagent concentration irrespective of the valency. If the sorption rate is governed by ion-exchange the compound formed differs from that formed by the ordinary chemical reaction, e.g., in the sorption of xanthate by partly oxidised galena one valency of the lead ion is bound to a xanthate ion and the other to the galena lattice. For effective flotation under normal conditions formation of stable adsorption layers is indispensable, but this is undesirable in selective flotation with depressants. Improved selectivity may be obtained by a judicious combination of methods, including the action of ultrasonic waves, high-frequency currents, high temperatures, and abrasive action to clean mineral surfaces.

The generation of gas bubbles and their discharge from solution may considerably increase the efficiency of a flotation process; bubble formation takes place on a much wider scale than is generally believed in mechanical flotation machines and is especially pronounced in vacuum flotation. Basic equations defining the thermodynamics and kinetics of bubble formation proposed by Klassen (6) show the dependence of flotation and over-saturation of the solution, frother concentration, and hydrophobicity of the mineral surfaces. Experimental application of these principles confirms that, for mineral particles of  $5-10\mu$ , separation is improved by vacuum flotation.

The activation of sphalerite by copper salts is shown by tracer methods to be due to replacement of zinc ions by copper ions in its lattice (7), which is rapid until three layers of zinc ions are replaced and then proceeds by the parabolic rate law. De-activation is due to sequestration of the copper ions in solution, but the copper complex formed must be considerably more stable than the corresponding zinc complex to be effective. In the selective flotation of lead zinc sulphide ores the degree of selectivity obtained depends upon gangue composition, degree of oxidation of the minerals and grinding conditions (8); zinc depressants have only a moderate effect but metallic iron abraded from the grinding mills tends to depress sphalerite, while the presence of oxidised lead minerals tends to activate it, possibly by ion-exchange in the surface layers. With some ores a better recovery of zinc in a higher grade concentrate is obtained by floating with diphenylguanidine instead of potassium ethylxanthate; generally diphenyl and dibutyl derivatives of urea and of guanidine are excellent flotation collectors (9).

Considerable work has been done in the United States and in Russia during recent years on the beneficiation of iron ores by flotation. Laboratory tests in a Hallimond tube show that operating at elevated temperatures improves the selectivity and the grade of

concentrates obtained in the soap flotation of iron ore (10). The floatability of goethite has been determined and correlated with its electrokinetic properties as determined by streaming potential measurement (11). In the separation of fine haematite and goethite from a quartz and chert gangue by soap flotation the pH of the pulp determines whether the gangue or the iron minerals are floated; floating of the latter is completely inhibited by slimes, but when the iron minerals float the selectivity depends on the structure of the fatty acid collector, the more saturated fatty acids from fish oil giving the best results (12). With oxidised white spirit as a collector and a tall-oil emulsion in combination with a soap, a high recovery of a good grade of iron concentrate has been obtained from low-grade limonite ores in Russia; the same reagents have been used with success in the recovery of 35-40% manganese concentrates from the slimes from the gravity concentration of manganese ores (13). Crude tall-oil emulsified with fuel oil is a good collector for Norwegian ilmenite flotation, giving a good recovery of high-grade concentrate from deslimed ore (14).

In the field of electrostatic separation Russian work (15) has shown that the relative conductivity of minerals ( $\gamma$ ) depends largely on the humidity ( $p$ ) of the ambient air and can be expressed by the equation:  $\log_{10} \gamma = -a \div bp$  where  $a$  and  $b$  are constants. The surface conductivity of dielectric minerals is determined mainly by the amount of water adsorbed on their surface so that the relative conductivities of associated minerals may change with the moisture content of the air. Hence either a dry or wet separation may be the most effective or it may be necessary to treat the mineral surfaces with reagents which modify their hydrophobicity. The theoretical principles of this process are similar to those of treating minerals with reagents prior to flotation so that further developments should follow from a fuller application of the accumulated knowledge of the latter process. Work at the U.S. Bureau of Mines (16) has shown that most minerals suffer an irreversible change in electrical conductivity when heated to a temperature between 100° and 800° due to alteration of adsorption layers, volatilisation of ions from the surface, or oxidation or reduction. Efficient electrostatic separation of gravity concentrates containing columbite, cassiterite, monazite, xenotime, orangite, and zircon has been obtained by feeding the sized material to the rolls at temperatures above 100° (17).

Two new types of wet magnetic separator for feebly magnetic minerals have been described: one (18) functions by means of an automatically operated cycle of frequency and collects the magnetic particles on grooved plates in a magnetic field, cleans them with a pulsed stream of water, and then removes them from the plates by a decrease in magnetic field strength and an increased water velocity; in the other (19) the paramagnetic particles are



retained in a 'magnetic corridor', the diamagnetic particles being washed out by a lateral current of water or by centrifuging.

### **Roasting, sintering, and fluidised bed techniques**

Davies (20) draws attention to the fundamental concept of sintering as a heat transfer process in which the ignition heat is continuously transferred through the bed as a heat wave initiating endothermic changes, the energy requirements of which are supplied by combustion of the fuel in the bed. Ideally the heat wave should be generated by the ignition hood followed by preheating of the incoming air, and the fuel content of the bed should be no more than that required to balance the endothermic changes; in practice, however, the heat wave is deficient in energy and this is offset by the excess fuel in the bed. Hence the quality of the sinter is reduced, more fines are returned and fuel is wasted. Sintering speed, i.e. the heat wave velocity, is a function of the rate at which incoming air acquires heat from the cooling sinter and imparts it to the unburnt feed below the combustion zone and is, therefore, a function of the rate of air flow and dependent on the bed permeability. The application of these principles to the sintering of taconite concentrates is discussed. Some German work (21) on the sintering of iron ores indicates that the process is connected with the advanced melting of the ore and the formation of new crystals, while the gangue is converted into a ferrous silicate glass which can be transformed to fayalite by annealing. The sintering temperature of ores with a mainly silicious gangue is between 1400 and 1560° according to the amount of slag-forming constituents present, but may be reduced to 1250° by adding lime. Ball (22) has studied the effect on the sinter strength of introducing excess air, both through the burner and by induced draught, during ignition of a low-grade sinter mix, the extent to which carbon goes into solution during inert ignition, and the effect of introducing excess air to inhibit this endothermic reaction. He also reports (23) the results of an assessment trial on a Dwight Lloyd sinter strand recently installed in a North of England ironworks. New features of this plant include means for using preheated air for sintering after ignition, constant-weight feeders for controlling raw material input, a quenching trommel for cooling return fines, and a Davidson cellular-type dust collector.

To avoid dusting losses, Stark (24) advocates mixing fine iron ore concentrates with a binder, agglomerating by means of a pugmill-extruder as used in the ceramic industry, firing the agglomerate at high temperatures, and cutting the resulting solid columns into convenient sizes for handling. Work at the U.S. Bureau of Mines (25) indicates that it may not be necessary to sinter taconite concentrates for blast furnace smelting. Pellets made from taconite fines with 1% of bentonite gave dusting losses

in smelting of only 43 lb. per ton compared with 7 lb. per ton for sinter, and there was no significant increase in coke consumption. Difficulties sometimes encountered in sintering iron ore flotation concentrates are attributed partly to the flotation reagents and partly to the particle size of the material (26).

In sintering lead ore concentrates the substitution of an up-draught for the usual downdraught increases the output of the plant, reduces the power consumption, and results in a higher sulphur dioxide content of the gases (27).

Fluidised bed roasting of sulphide and other ores continues to attract attention and the process has been extended to the reduction treatment of iron-bearing minerals. For roasting antimony sulphide concentrates (28) a shallow cylindrical chamber with a conical bottom is used to contain the charge, the air with the mineral in suspension being injected into the apex of the cone after the chamber has been preheated to 600–700°; efficient eddy currents in the cylindrical section prevent settling of roasted or partly roasted material into the cone and carry all the calcine out of the top of the furnace to be collected in the dust-collecting plant; the antimony is all converted into  $\text{Sb}_2\text{O}_3$  and not into the unwanted  $\text{Sb}_2\text{O}_4$ . Fluosolid roasting of low-grade antimony ores and tailings has been used in Russia to obtain sublimes with over 30% Sb from feed containing around 1%; antimony recovery consistently exceeds 80%, and the product is used for producing the metal electrolytically (29). A two-stage fluosolid roasting process to recover arsenic compounds from arsenopyrite and to eliminate arsenic from pyrite calcines leaving an iron oxide suitable for steel manufacture is described by MacAskill (30); a similar plant is used for roasting pyritic gold concentrates (31). With a fluosolid reactor maintained at 690° it is possible to convert about 95% of the copper content of a pyritic concentrate (20% Cu) to water-soluble copper sulphate (32).

In the roasting of siderite in shaft furnaces, when material finer than about 5 mm. is present, the increased resistance of the charge to the air flow and the irregular air distribution in the furnace reduce the capacity of the furnace and lead to a deterioration in the magnetic properties of the roast. Pilot plant tests (33) have shown that the fluidised bed process produces from Siegerland siderite a more homogeneous product which behaves much more satisfactorily in the subsequent magnetic separation.

The New Jersey Zinc Co. (34) use the fluidised bed technique to roast zinc ore to give a calcine free from cadmium and lead. The roaster comprises two superimposed beds, the lower being mildly agitated and the upper more vigorously agitated and maintained at 1050°; agglomerated concentrate is fed to the bed, zinc sulphide being roasted to oxide in the lower zone, and lead and cadmium sulphides volatilising from the upper.

New Zealand iron sands can be reduced to sponge iron in a fluidised bed after previous oxidation at 1050° in air. For the reduction carbon monoxide at 600-700° or hydrogen-rich gases at about 900° can be used (35); the impurities present retard the rate of reduction but prevent agglomeration.

Russian work (36) has shown that volatilisation of rhenium in the roaster gases is well over 90% in fluidised bed roasting of molybdenite compared with about 65% in muffle roasting and under 50% in a rotary kiln; scrubbing the gases with water or potassium chloride solution effectively recovers the volatilised rhenium.

The segregation process of treating low-grade oxidised and mixed oxide-sulphide ores for the recovery of copper has been studied in detail on different ores with various types of gangue (37). The ore is heated with a small quantity of NaCl and 0.5-1% of coke at 700-750° in a non-oxidising atmosphere to produce fine flake copper which is subsequently recovered by flotation. The process has considerable merit for the recovery of copper from highly calcareous ores and for silicious ores not amenable to conventional treatments. Recoveries of over 80% of the copper from a complex oxidised ore having a dolomitic gangue containing much pyrolusite and goethite have been obtained in Peru by heating a pelletised mixture of the finely ground ore, salt and coal at 750° in a shaft furnace with hot neutral gases from the combustion of oil, quenching the pellets, lightly wet grinding the sludge, and passing the pulp to flotation cells (38).

### Hydrometallurgy

Pressure leaching under oxidising conditions, originally applied to pyritic ores of copper, nickel and iron, has been adapted to the treatment of copper-nickel matte (39), zinc sulphide concentrates (40) and galena (41). Finely ground matte behaves in the ammonia pressure-leach process like a nickel-copper sulphide flotation concentrate, but there is a much smaller quantity of iron to be removed. Treatment of zinc sulphide concentrates in 12% sulphuric acid at 110-115° in an autoclave with air results in more than 95% of the zinc dissolving as sulphate. The solution is treated by conventional methods to recover high-purity electrolytic zinc and the acid liquors are recycled. The process eliminates roasting and ferrite formation, and recovers elemental sulphur. Pressure oxidation of galena concentrates in acid solution converts the lead into the insoluble sulphate and eliminates other metals as soluble sulphates. On leaching the sludge with a solution of diethylenetriamine as much as 650 g. of lead per litre dissolves, and passage of carbon dioxide through this solution precipitates pure basic lead carbonate free from other metals which form amine complexes.

Reduction of the carbonate with carbon yields silver-free lead of better than 99.99% purity. The amine is regenerated by treatment with lime.

Uranium can be extracted from pyritic shale by pressure leaching with dilute sulphuric acid generated by internal oxidation of the pyrite with oxygen (42). Leaching of various uranium ores with acid and alkaline reagents is described, the oxide being recovered by ion-exchange or solvent extraction. Using Amberlite IRA-400 anion-exchange resin to strip acid leach liquors, Canadian workers (43) removed the uranium completely from the resin with sodium carbonate or bicarbonate and recovered it by precipitation with sodium hydroxide; only slight deterioration of the resin was noted after 50 cycles of loading and elution. The uranium ores of Wyoming are leached with sulphuric acid when the soluble lime content is less than 6% or with sodium carbonate when it is more; from the acid leach uranium is removed by solvent extraction and the alkaline leach is used to strip the uranium from the solvent (44). A catalytic reduction process (45) has been devised for the direct precipitation of pure uranium tetrafluoride in a dense crystalline form directly from the solutions obtained from the solvent extraction strip; the dehydrated product can be used directly for production of the hexafluoride or for reduction to pure metal.

The effluent from the ion-exchange plant used in the recovery of uranium from certain Canadian ores contains 0.15–0.25 g. of thorium per litre; solvent extraction with a 5% solution of di-tridecylamine in kerosene recovers more than 95% of the thorium, which can be stripped from the solvent with sodium carbonate or chloride solution to yield a product with more than 98% of thorium (46). Similar results are obtained with di-(2-ethylhexyl) hydrogen phosphate in kerosene (47). The extraction of thorium from monazite sand is considered in several papers in which the acid and alkali methods for decomposing the sand are discussed and chemical and solvent extraction processes described for recovering the thorium, uranium and rare earths. Extraction from a nitrate solution with tri-*n*-butyl phosphate in xylene or kerosene is the most efficient procedure for recovering the thorium if ferric nitrate is added to prevent interference of any phosphate present (48); if the cerium is present as ceric nitrate both cerium and thorium pass into the solvent, but the cerium is readily removed by a reducing strip (49). A good review of the subject is given by Buddery *et al.* (50). Madyan (51) reports that with a 1 : 1 ratio of solvent to aqueous solution, extraction of thorium is almost complete from 0.1 M solutions of the sulphate with 1.0 M solutions in kerosene of trimethylnon-4-yl phosphate at pH 1–2.5 or diethyltridec-6-yl phosphate at pH 3–9, whereas di-(2-ethylhexyl) phosphate solutions extract only 87%; the thorium can be recovered by stripping with

sodium carbonate. In a two-cycle process for recovering both thorium and uranium from monazite sulphate liquors the former is extracted with a primary amine in a hydrocarbon oil and the latter with a secondary or tertiary amine (52); amine extraction is more selective than ion-exchange for recovering uranium (53).

Thorium is preferentially adsorbed on passing a sulphate solution of monazite through columns of cellulose phosphate (54) from which it can be subsequently eluted with 10% ammonium carbonate solution; ferric salts must first be reduced with aluminium. Although this procedure is interesting from a technical point of view it is doubtful whether it can compete economically with solvent-extraction processes.

Much interest has been shown in America in methods of recovering the rare earths from bastnäsite and euxenite. A nitric acid attack of the former after calcination, followed by solvent extraction of the ceria, gives good recoveries of the rare earths (55), but the best procedure is to digest the ore with sulphuric acid to remove fluorine and most of the silica, calcine the sulphated product at 650° to render the gangue constituents insoluble (56), and leach the calcine with water to extract the rare earths. The hydroxides are recovered with hot caustic soda, washed, air-dried at 110° and leached with dilute hydrochloric acid to extract the trivalent oxides, and pure ceria finally recovered as basic nitrate (57) or by extraction into tributyl phosphate and stripping with dilute sulphuric acid (58). Techniques have also been worked out for extracting cerium (IV) directly from sulphate leach liquors (59) and for the subsequent partial separation of the rare earths using long-chain primary amines as solvents (60). A comparatively simple process for recovering all the valuable constituents of euxenite consists of high-temperature chlorination of the mineral in presence of a carbonaceous reducing agent to remove titanium, niobium and tantalum chlorides (separated by fractional condensation and solvent extraction), and to collect the iron and uranium as a  $\text{NaCl-FeCl}_3\text{-UCl}_4$  eutectic; the thorium is finally extracted from the residue of rare earth chlorides by solvents (61). Various methods for the treatment of the chloride solution to separate the earths have also been studied (62), particularly solvent extraction with tri-*n*-butylamine-3-methyl-2-butanone (63).

### **Ferrous metallurgy**

Investigations in this field during the last two years were mainly concentrated on direct reduction processes and the use of oxygen in steel making.

The Republic Steel-National Lead process has proved successful in reducing iron ores with 30-65% of Fe to produce metallic iron briquettes with more than 99% of iron in a rotary kiln using solid

carbon fuels with up to 7% of sulphur. The briquettes contained less than 3% of  $\text{SiO}_2$  and less than 0.05% of sulphur; more than 90% of the phosphorus content of the ores was rejected (64).

The reduction of fine iron ores suspended as a dispersed cloud in hydrogen has been studied by Ezz & Wild (65), who determined the effect of particle size and shape, the nature of the ore and its porosity, temperature, and ore-gas ratio on the rate of reduction. Cavanagh (66) has critically reviewed the technical and economic aspects of the various methods proposed for the direct reduction of iron ores.

Recent American developments in the use of oxygen in duplex and stationary open-hearth furnaces are discussed by Pearson (67), who also illustrates modern designs of furnaces with acid and basic roofs and gives details of their operation. Progress in the use of oxygen in a modified tilting furnace is reported (68) and Chater & Charles (69) have described tests on oxygen lancing in the ladle and the effects of introducing limestone and soda into the oxygen stream. By feeding oxygen into the mouth of a rotating cylindrical furnace containing pig iron the sulphur is efficiently removed and the metal has a low hydrogen content. The chemical and thermal effects of introducing oxygen into the open-hearth furnace are discussed by Hodge & Arnold (70). A British patent (71) claims that, by blowing a perpendicular jet of oxygen on to molten pig iron so as not to agitate the surface, all the main oxidation processes can be conducted without the slag acting as an intermediary and with the use of less than 25 kg. of lime or flux per ton of metal. By using a rotating furnace at relatively high speed and blowing in oxygen from the top it is possible to remove most of the phosphorus from pig iron as a pourable slag rich in phosphorus while leaving about 0.5% of C in the metal (72); the slag is removed and refining completed with a new slag.

Low-grade ferruginous manganese ores can be utilised for the production of spiegeleisen and high-grade ferromanganese by a duplex smelting process in a submerged-arc electric furnace (73); the ore is first smelted to produce the spiegeleisen (12% Mn) and a manganese-rich slag (54% Mn) and the latter is resmelted with low-grade ore to produce ferromanganese (76% Mn).

## Copper

A direct smelting process for producing copper from flotation sulphide concentrates has been developed in Japan; the concentrates are fed through a specially designed hopper into a side-flue type blast furnace to make effective use of the heat of combustion of the sulphur and iron. Fuel consumption is reduced, no preliminary treatment of the concentrates is required and the flue gases can be utilised directly for producing sulphuric acid (74). The

factors affecting copper reverberatory furnace performance and their influence on the choice of smelting methods are critically reviewed by Verrey (75), and the influence of charge composition upon the heat requirement in copper matte smelting is discussed by Evans (76).

### Nickel

By smelting garnierite with phosphate rock, gypsum and coke at 1350°, more than 90% of the nickel can be recovered in the matte and the phosphatic slag contains 16-19% MgO and 12-17%  $P_2O_5$ , more than 97% of the latter being citrate-soluble (77).

The nickel oxide produced in the hydrometallurgical treatment of Cuban ores can be reduced to sponge nickel by heating a 20 : 5 : 1 mixture of the oxide, fine anthracite and dolomite in saggars in a tunnel kiln; pilot plant tests on a tonnage scale have yielded ingot metal with Ni-Co 98.5%, Fe 0.7%, S 0.06% and C 0.07% from smelting the sponge in an electric or basic open-hearth furnace (78).

### Magnesium

Thermo-chemical and -dynamic studies on the production of magnesium by reduction of burnt dolomite with ferrosilicon (79) have shown that the first reaction, starting just above 800°, is the reduction of lime to  $CaSi_2$  and  $Ca_2SiO_4$ , which is slow below 890°, at which temperature eutectic formation causes the reaction to accelerate; above 1020° the  $CaSi_2$  melts and the calcium vapour formed reduces the magnesia to magnesium vapour, the rate of reduction increasing with rise in temperature up to 1450° and then decreasing due to melting of the charge and decrease in porosity of the briquettes. Reduction of magnesium chloride with calcium carbide is complete at about 1000° *in vacuo* in a very short time, whereas silicothermic reduction of the oxide requires a fairly long heating at 1400-1500°; the carbide process might be made economical by using the calcium chloride produced to convert magnesia to chloride in the presence of carbon dioxide and then using the calcium carbonate produced as a source of carbon dioxide and calcium carbide (80).

### Zinc

Indian investigators (81) report that a high recovery of zinc can be obtained by heating at 1050° briquettes composed of carbon and a 1 : 1 molar mixture of zinc blende and ferric oxide, the iron being converted into ferrous sulphide. The use of peat semi-coke as a reducing agent in the retort process of producing zinc gives better recoveries of the metal with a smaller amount of reducing agent in the charge (82). Two accounts of the operation of the blast

furnace process for the recovery of zinc and lead from mixed calcines have been published (83, 84).

Japanese workers (85) claim that the presence of manganese in the sulphate electrolyte used for the production of electrolytic zinc prevents disintegration of the lead anode (1% Ag) and the formation of excessive anode slime by producing a thin film of manganese dioxide on the anode. Electrolytic zinc has been successfully prepared from sulphate electrolytes containing chlorides by the use of cast magnetite anodes which resist attack both by chlorine and oxygen (86).

### Aluminium

The extraction of cell-grade alumina from minerals other than bauxite continues to attract attention but pilot plant operations have not yet indicated that alumina so produced can compete in cost with that obtained from bauxite by the Bayer process. By baking shale with concentrated sulphuric acid the alumina, ferric oxide and potash are sulphated, leaving the silica insoluble; from the leach with hot mother-liquor containing potassium sulphate potash alum is crystallised and then purified by extracting the iron from its solution with a kerosene solution of Primene, the purified alum is roasted, sulphuric acid being recovered from the gases, the alumina is leached, and potassium sulphate is recovered from the solution, the mother-liquor being recycled (87). The lime-soda sinter process has been applied to the recovery of alumina from anorthosite (88) but the cost per unit of alumina is 50% above that for treating bauxite, although some revenue might be obtained by using the residues in cement manufacture. Very close control of the sinter composition, of the time and temperature of sintering and of the leaching operation is required to avoid difficulties in filtration of the aluminate liquor and of the recovery of alumina therefrom in high yield (89). According to Zoccheddu (90) hydrous silicates, such as kaolin, if relatively free from alkaline earths and fluorides, decompose to give a high yield of acid-soluble  $\gamma$ -alumina if roasted at 850° in the presence of salt as a catalyst.

A study (91) of the anode polarisation in aluminium reduction cells has shown that, with good anode current distribution, no fluorocarbons are formed but, when there are large distances between anode and cathode, concentration polarisation develops as the bath becomes depleted in alumina and continuous local generation of  $CF_4$  may then occur. For the production of super-pure aluminium a circular three-layer cell has been developed in Germany (92); it has two fore-wells and two side-channels at 90° to one another, at the widened ends of which the refined metal is solidified and in which the cathodes are embedded so that the p.d. between the cathode conductor and the metal is reduced from



about 0.6 to 0.05 V. With 99% aluminium as the feed the cathode metal is better than 99.999%, the impurities being of the order of 1-2 p.p.m. each of Cu, Fe, Si, Ti and Zn; this metal is more than 10 times as resistant to corrosion by 10% HCl as the 99.99% grade.

## Titanium

Titanium tetrachloride for the production of the metal is generally obtained by chlorination of rutile, but recently attention has been given to the possibility of obtaining it from the much more abundant ilmenite. According to Ostberg (93) after reduction of roasted ilmenite with carbon monoxide at 1100-1200° the sponge iron and  $TiO_2$  can be separated by mechanical means, the  $TiO_2$  concentrate obtained being suitable for direct chlorination. Arc-furnace smelting of Idaho ilmenite sand produces iron and a titanium-rich slag; by grinding the slag to 200 mesh, forming it into coked briquettes with 35% of carbon, and heating these at 600-850° in a shaft furnace in a current of chlorine, commercial-grade  $TiCl_4$  can be obtained in high yield with some  $NbCl_5$  as a by-product (94). The chlorination of titanium minerals with carbonyl chloride and with mixtures of chlorine and carbon monoxide has been studied by Dunn (95); the chloride is more effective than the gas mixture at temperatures up to 600°.

By chlorination of niobium-bearing, coke-reduced ilmenite at 400-500° and passage of the vapours through heated purification columns a good grade of  $TiCl_4$  has been obtained directly and  $NbCl_5$  recovered from the columns (96). A trap for collecting preferentially the ferric chloride and other impurities less volatile than  $TiCl_4$  produced in the chlorination of ilmenite depends on the formation of low-melting-point mixtures of  $FeCl_3$  and NaCl of near eutectic composition (97); practically no iron passes the trap and the condensed  $TiCl_4$  is free from suspended impurities.

Treatment of the solution obtained by dissolving ilmenite in sulphuric acid with HCl and KCl at 0° precipitates crystals of  $K_2TiCl_6$ ; the dried salt yields  $TiCl_4$  when heated at 300-500°, or it may be directly reduced to titanium by magnesium or hydrolysed to the dioxide (98).

The reduction of titanium tetrachloride by sodium has been intensively studied at the U.S. Bureau of Mines during recent years. The reaction occurs in stages, lower chlorides first being formed. At 100-200°  $TiCl_4$  reacts with molten sodium dispersed on an agitated bed of sodium chloride to form  $TiCl_3$  and  $TiCl_2$  (99), which at higher temperatures form a solid phase with sodium chloride while the excess sodium forms another solid phase with NaCl; these two phases then react to produce crystals of titanium, the reaction being of an electrochemical nature. The reaction is complete at 800° and the resulting metal is of high purity, having,

when melted, a Brinell hardness of 50-60 (100). Several British patents based on this reaction have been granted (101-104).

Among the electrolytic processes which have been proposed for the production or refining of titanium are electrolysis of the carbide in a fused salt bath (105) and deposition on an induction-heated cathode from a solution of  $\text{TiCl}_3$  in the fused  $\text{KCl-LiCl}$  eutectic (106). For electrorefining an internally heated fused salt bath is claimed to be superior to one externally heated (107). An electrolytic cell for the production of titanium in which  $\text{TiCl}_4$  is continuously fed into a porous basket-cathode has been designed to avoid the fused salt electrolyte between anode and cathode from accumulating lower titanium chlorides which react with the brickwork of the cell and with atmospheric oxygen (108).

### Vanadium

Commercially produced vanadium has been refined by electrolysis in a bath of molten  $\text{NaCl}$  containing 3-6% V as vanadous chloride (109). Both the oxygen and nitrogen contents are reduced by 60-70%, and the resulting metal after argon-arc melting has a Rockwell B hardness of 35 compared with an initial 97. The ingots can be cold-rolled to 99% reduction before edge-cracking appears.

### Hafnium

Reduction of purified  $\text{HfCl}_4$  by a mixture of magnesium and sodium is claimed to give a purer product than that obtained with magnesium alone (110). Ingots produced from the sponge can be cold-rolled to sheet.

### Thorium

Chlorination of a bonded carbon thoria mixture in molten  $\text{NaCl-KCl}$  eutectic provides a simple way of producing a  $\text{ThCl}_4$  electrolyte from which a high-grade thorium powder can be obtained by electrolysis with a molybdenum cathode and graphite anode (111). According to Meyer (112) thorium produced by electrolysis of thoria in molten  $\text{KF-ThF}_4$  mixtures is superior to that produced from  $\text{KCl-NaCl-ThCl}_4\text{-ThO}_2$  mixtures, having a higher purity and larger particle size; the decomposition potential in both systems is 1.92 V. Both electrolytes can be used for electro-refining crude thorium metal to obtain reactor-grade metal, rare earths and other impurities being efficiently eliminated (113). The production of thorium by reduction of the oxide with calcium has been studied by Fuhrman *et al.* (114).

### Chromium

Considerable interest has been shown in recent years in the possibility of using chromium-based alloys for high-temperature

applications and this has led to extensive studies of the electrolytic production of the metal in high purity and at improved current efficiencies. Pioneering work along these lines carried out in Australia for some years has given such promising results as to incite further studies in America. At the U.S. Bureau of Mines (115, 116) massive high-purity chromium deposits have been obtained by electrolysis of purified chromic acid solutions at 85-90% baths containing sulphate operated at only 13% current efficiency, whereas those containing fluoride or fluosilicate ions operated at 40-44% efficiency. Ryan (117), working on similar lines, obtained only 8-10% efficiency in sulphate-containing baths and 35-40% decreasing with time to a steady 25-30% in fluoride- or fluosilicate-containing baths. All these workers obtained deposits containing 50-150 p.p.m. of oxygen and about 20 p.p.m. of nitrogen with only minute traces of metallic impurities; the arc-melted metal was hot-worked to rod and sheet and drawn into wire ductile at room temperature.

Attempts to refine electrolytic chromium with high oxide content have been made in a fused  $\text{NaCl}-\text{CrCl}_2$  bath (118). Although the deposited metal contained only 2.5-10% of the oxygen and nitrogen in the anode metal it was seriously contaminated with iron or nickel from the cell walls.

### Tungsten

Metal of 99.7-99.94% purity can be obtained by electro-deposition at 950-1050 from solutions of impure tungsten compounds or of scheelite in fused alkali phosphate or borate baths containing sodium chloride to increase the bath fluidity and to flux the lime. In scheelite baths use of a rotating cathode and a low voltage results in preferential deposition of the molybdenum, 98%, being deposited with only 2% of the tungsten. Power consumption is 1-2 kWh per lb. of tungsten (119).

### High-purity metals

Zone-melting as a means of preparing high-purity metals continues to attract the attention of workers in this field and several patents covering apparatus for the zone-refining of metals have been granted in the last two years (120-125). Work has been published on the application of the process to iron (126), zinc (127), molybdenum (128), tungsten (129), niobium (130), nickel, titanium, vanadium, aluminium and gold (131), and lead, tin, bismuth and silicon (132), and the efficiency of zone-refining processes has been discussed by Davies (133).

The basic principles underlying the iodide dissociation process have been formulated by Looman (134) and its application to the production of pure niobium (135) and tantalum (136) described.

High-purity tungsten is obtained in the form of dense columnar crystals by hydrogen reduction of the hexafluoride (137) at 600°; the crystals have  $d$  19.25 (compared with  $d$  19.23 for hard-drawn wire made by conventional methods) and contain less than 0.01% of impurity. The purity of hafnium made by the Kroll process is considerably improved and the oxygen content reduced to 0.01–0.04% by passing the  $\text{HfCl}_4$  vapour through molten  $\text{KCl-NaCl}$  eutectic prior to reduction (138).

During the past years intensive work on the preparation of the rare earth metals, scandium and yttrium in a state of high purity has been in progress in the United States. At the Ames Laboratory yttrium has been made on a relatively large scale by feeding a mixture of yttrium fluoride and calcium chloride into molten calcium-magnesium alloy in a titanium pot in an inert atmosphere, crushing the resulting 73 : 27 yttrium-magnesium alloy, distilling off the magnesium at 950° in a vacuum, and vacuum-melting the yttrium sponge by the consumable-arc process (139). Sponge of 99.8% purity can also be obtained by reducing the chloride with sodium or lithium in a molybdenum crucible in an argon atmosphere (140); arc-melted ingots can be rolled into sheet which is ductile after annealing. Zone-refining in an electron-beam furnace increases the purity to better than 99.9%; the refined metal has m.p. 1495 ± 5° and can be cold-rolled to 90% reduction (141). Despite its relatively low vapour pressure, 100-g. batches of extremely pure yttrium have been prepared by distillation from tungsten or tantalum crucibles at 2200°,  $10^{-5}$  mm. Hg. This distillation process has also been used for preparing many of the rare earth metals, particularly dysprosium, thulium, terbium and holmium, as well as scandium (142), the metals being first obtained by calcium or lithium reduction of the fluorides in tantalum crucibles. The distilled metals contain 150 p.p.m. of oxygen. The three metals of the group which exhibit divalency, samarium, europium and ytterbium, are readily prepared in a very pure form by reduction of the oxides with metallic lanthanum or zirconium powder in a high vacuum at above 1200°, the metal distilling out of the mixture and being collected on a 'cold finger' maintained at 300–400° (143).

High-purity gallium can be prepared from commercial grade metal by dropping it in fine streams through ammonia heated at 800°; the impurities are converted into nitrides which form a scum on the molten metal (144).

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## PHYSICAL METALLURGY

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### Introduction

WORK on the properties of the more refractory metals accounts for a rapidly increasing proportion of the total research effort, and the *Journal of the Less-Common Metals* has facilitated the publication of much valuable material. Among the papers of general interest, that of Robins (1) deserves particular attention. Towards the centre of the transition series, where high metal valencies are possible, a tendency exists for the number of bonding electrons to equal half the effective co-ordination number. It is suggested that the alloying characteristics and crystal structures of the transition elements are dictated by the stability of this arrangement, which permits the maximum electron resonance contribution to the bond strength. Interstitial atoms will, for example, be attracted electronically to structural defects in tungsten or molybdenum but not to tantalum, which is to the left of Group VIA. Differences in the ductility of tungsten and tantalum can thus be explained.

Accurate analytical techniques are essential if the effects of interstitial impurities are to be properly evaluated. Until fairly recently the classical vacuum fusion technique has been considered above reproach but isotope dilution techniques give significantly higher oxygen and nitrogen values than this, and Pearce & Masson (2) conclude that vacuum fusion results for low oxygen values are seriously in error.

One of the more interesting secondary features of the general pattern of development has been the increasing use of, and interest in, physical and electrical measurements for following transformations or assessing metallurgical conditions. Particularly serious problems are raised by the number of conferences and volume of literature on the magnetic properties of metals and alloys (see Supplementary Bibliography). The single domain theory dominates most of the work on high coercivity alloys, and the construction of permanent magnets from fine powders stems logically from this type of conception. A theoretical study by Stacey (3) casts doubts on the complete validity of the presently accepted single domain inclusion theory, which does not explain why thermal agitation should not cause spontaneous decay of remanence in a very short time.

The measurement of residual electrical resistance at low temperatures is a sensitive method of studying impurity levels, vacancies, dislocations and lattice deformations (4). Differences in impurity level which would be difficult to detect by conventional techniques are simply demonstrated by comparing the respective resistance ratios at the boiling points of hydrogen and nitrogen (5-7). The practical implications of this technique have not yet been fully appreciated.

### Fatigue

Some materials harden under cyclic strain conditions, while others soften. Recent studies of the relationship between strain hardening and fatigue have resolved some of the anomalies and remarkably unanimous results have been reported. Thus, fully annealed material invariably hardens during fatigue until a fairly constant hardness is achieved. Providing the tests are carried out at constant stress the extent of hardening is largely independent of the stress level (8) and occurs with polycrystalline material during the first few thousand cycles. While Ebner & Backofen (9) reported saturation in single crystals of copper after 2000 cycles, Kemsley, with polycrystalline copper, did not achieve steady hardness values even after  $10^4$  cycles (10). Crack formation was associated with the onset of saturation (9) but Kemsley reported that failure did not occur before fairly constant hardness values had been arrived at. Tests at constant strain amplitude (11) indicated that fatigue failure frequently prevented the attainment of a steady hardness.

The applied stress is the factor which determines whether work-hardened material softens or hardens during cyclic stressing. If the cyclic stress is below a critical value, work-hardened material softens and fully annealed material hardens until both materials approach a similar hardness value (10, 11). The recovery induced by cyclic stressing is reflected in lower tensile strengths and sharpened X-ray diffraction patterns.

The hardening induced by fatigue is different in character from that caused by unidirectional deformation (8, 10, 12). Softening temperatures are higher, and the shape of the annealing curves suggest the possibility of a multi-stage recovery process. Fatigue-hardened copper has creep properties at 300° superior to those of copper statically work-hardened to the same extent (8). Precipitation experiments (13) have demonstrated in a striking manner the differences between cyclic and unidirectional hardening.

While cold rolling did not alter the character of precipitation from a supersaturated aluminium-magnesium alloy, fatigue hardening modified the Widmanstätten structure normally observed to a very fine dispersion. Holden (12) found that fatigue hardening completely suppressed the yield point phenomenon exhibited by

annealed mild steel specimens. Broom & Ham (14), who reported pronounced yield-point effects in fatigue-hardened single crystals of copper, observed that grain boundaries would probably obscure the effect. Static tests on single crystals, carried out after fatigue hardening at room temperature, showed that deformation in the regions between striations began at stress levels higher than the maximum stress supplied during fatigue. Holden reported that the initial deformation occurring after cyclic hardening resulted from slip which was restricted to zones which had been active during cycling. The agreement between these results suggests a clear line of demarcation between the properties of the fatigue striations and those of the relatively hard matrix. The yield-point effects indicate that point defects form obstacles to dislocation movement in cyclically hardened material, which exhibits slip phenomena similar to those observed in irradiated metals (8, 12).

Negative strain rates sometimes occur on unloading in creep experiments on polycrystalline metal specimens. The effect, which does not occur in single crystals, is often explained in terms of grain boundary behaviour or the uneven deformation of a polycrystalline aggregate. By applying cyclic stresses ranging up to 4.5 kg. cm.<sup>2</sup> Meléka & Dunn (15) induced appreciable recovery into single crystals of zinc, thus suggesting that the 'after effect' had its origin in the grain interior. Recovery halted when the fatigue stress was removed.

Although grain size has a considerable influence upon the cleavage fracture of materials tested under static tensile conditions, rotating beam tests on polycrystalline zinc (16) showed no correlation between endurance limits and tensile fracture results. The findings of Meléka & Dunn (15) suggest that cyclic stresses can impart mobility to dislocation 'pile-ups', thus preventing high stress concentrations, so that any tendency towards grain size dependence would be minimised. Holden's (12) results tend to support this hypothesis. Fatigue-hardened steel subsequently tested under static tensile conditions exhibited its original grain size dependence, even though deformation was restricted to zones which had been active during cycling. Thus, in the absence of a cyclic stress nothing prevents the dislocation pile-up required for grain size dependence.

In contrast to the detailed work on fatigue hardening, the factors immediately preceding and leading to fracture have been rather neglected. Crack formation occurs during the first 5% of the total fatigue life and intermediate annealing has no effect upon the number of cycles to failure (17). Even when push-pull conditions ensure a uniform stress distribution over the cross-section, cracks originate at the free surface and are accelerated by atmospheric conditions (17). Coatings of long-chain polar substances greatly increase the fatigue strengths of steel, magnesium and beryllium.

copper alloys (18). The tightly packed monolayers formed on the metal surface by the polar compounds are thought to act as barriers to water and oxygen molecules, compounds having 12 carbon chains providing the optimum conditions; although the type of polar group is less important than the number of carbon atoms in each molecule. The presence of oil on the surface of a fatigue specimen has a harmful effect (18a), but this can be partially or completely eliminated by protecting the surface with rubber or neoprene. Specimens so protected and subjected to static triaxial compression are more resistant to additional fatigue stresses than those tested under normal atmospheric conditions, probably because material subjected to triaxial tension is less resistant to fatigue.

Fatigue failure at low stresses seems to be caused simply by the notch effects which originate when slip bands reach a free surface (19). With the aid of a simple taper section technique, Wood concluded that point defects facilitated the formation of fatigue fissures by extension of the notches produced at the head of a slip band. Mott (20) proposed that dislocations which moved in one direction along a certain path and returned by a different one, so maintaining a fixed circuit, could lead to surface extrusions or intrusions, but the possibility of return journeys along paths which are randomly varied over a width comparable to that of the slip band has also been suggested (21). This random slip results in surface roughening and consequent stress concentrations which confine subsequent slip to surface valleys. The mathematical model set-up suggested that  $1.3 \times 10^5$  cycles would be required for a surface valley to develop into an incipient crack. As the number of cycles needed to induce failure is at least twenty times that required to induce incipient cracks (17), the mathematical basis may need considerable modification.

The sub-structure developed by fatigue has been directly studied by thin-film electron-microscopy (22). Dislocation arrays similar to those produced by polygonisation were observed, and serrated grain boundaries were a characteristic feature. A cellular network of dislocations was typical of fine double slip. Heavy defect concentrations on some sub-boundary zones might have been embryo voids or cracks.

Thermal fatigue studies (23) show that heating shocks are more damaging than cooling shocks between the same temperature limits. The cracks produced originate at the surface, are inter-crystalline, and exhibit the characteristics of creep rather than fatigue failure. Air accelerates thermal fatigue failure, and greater endurance is achieved in an inert atmosphere.

### Creep

Problems of grain boundary behaviour dominate much of the

recent research on creep, although the results appear as yet to have few practical implications. Intrater & Machlin's work on copper bicrystals (24) permits a clear distinction to be made between 'pure' grain boundary sliding and sliding which occurs by plastic shear deformation in a zone adjacent to the grain boundary. 'Pure' grain boundary sliding occurs by a series of extremely rapid jumps of about one micron. Inter-crystalline cracks are formed after testing in vacuum, and isolated inter-crystalline voids after testing in hydrogen. The area covered by these voids and cracks increases with the extent of sliding. Zone shear is two to three times as rapid as pure sliding. It produces more voids and the incubation period in zone shear is absent in grain boundary sliding.

Considerable difficulties are involved in extending results of this type to polycrystalline aggregates. The relative importance of grain deformation and grain sliding during the tensile creep of aluminium has been studied by Rachinger (25). At 300° the surfaces of polycrystalline specimens deform by grain elongation, while the interior deforms by sliding. Observations of the surface grain boundary movement are unlikely, therefore, to be representative of interior movement. This effect is of most consequence in fine grained material, where the sliding of individual grain boundaries, although small, contributes a high proportion of the total elongation (26). Such conclusions diminish the value of Brunner & Grant's careful study of grain boundary sliding, which depended upon external microscopical examination (27). These authors found that grain boundary sliding, which increased with temperature, could account for up to 10% of the total strain observed. The proportion of grain boundary sliding to total elongation decreased as the stress and total elongation increased. If little correlation between interior and exterior grain boundary movement exists, Reinacher's (28) elegant device for creep-testing noble metal specimens on the hot stage of a microscope will be of limited utility.

Grain boundary migration minimises or even prevents void formation in some instances. Copper tested in vacuo under conditions of low boundary mobility gave inter-crystalline fractures and low elongation. At higher temperatures, when grain boundary migration was rapid, ductile trans-crystalline fractures resulted (29). The function of oxygen or oxide in retarding grain boundary migration has also been emphasised, and in lead (30) segregation of oxygen to the grain boundaries appears to be a controlling factor. When grain boundary movement in pure chromium was hindered by oxide particles (31) the resultant stress concentrations opened up nuclei cavities which grew to form rounded voids. Seigle (32) has advanced a hypothesis to account for the inter-crystalline cracking which occurs when no boundary sliding or shearing can be detected. Based upon a flow of vacancies from grain boundary to crack edge,

the mechanism must be distinguished from earlier theories because of its emphasis upon the role of grain boundaries as vacancy sources.

The general tendency to attribute practical improvements in creep resistance to strengthened grain boundaries must be viewed against this background, and considerable confusion still exists. By heat treating Nimonic 80A type alloys so as to produce a coarse grain-boundary carbide segregation, Weaver (33, 34) obtained improved high-temperature properties. The large particles of carbide, it was postulated, restricted the cavities formed by grain boundary sliding and prevented them from spreading. Their effectiveness in preventing triple point cracking at high stresses could be interpreted in terms of Stroh's formula for cleavage fracture, or by Inglis' treatment for crack growth (59). Other workers have found, however, that continuous grain-boundary precipitates are definitely harmful (35) and reduce fatigue, ductility and impact properties. The decisive factor, the ratio between carbon content and grain boundary area, was neglected by Weaver, whose conclusions on the effect of trace additions of boron and zirconium conflict with those of Decker & Freeman (36). The beneficial effects of these elements are attributed by the latter investigators to the fact that they retard the agglomeration of carbide particles at the grain boundaries. Weaver suggests that carbides, boron and zirconium operate on the grain boundary in a complementary manner whereas Volk & Franklin suggest a simple strengthening effect (37). Larger quantities of boron improve the high-temperature properties of cast austenitic alloys, and above 800° the network of borides which adversely affect room-temperature ductility become relatively mobile and capable of following the flow pattern of the matrix (38).

Creep tests on iron under fluctuating temperature conditions emphasise in a spectacular manner the decisive influence of grain boundary behaviour (39). Commercial iron was heated under conditions in which the carbon-rich grain boundary regions in the centre of the gauge length remained in the  $\gamma$ -range throughout the experiment, while the grain-boundary regions in the cooler parts of the specimens underwent repeated  $\alpha$ - to  $\gamma$ -transformations. This resulted in the formation of two necks, symmetrically disposed on both sides of the hot zone. Pure iron of low carbon content, tested under the same temperature and stress conditions, developed one neck only at the centre of the test piece.

Intercrystalline voids in iron and nickel-chromium alloys are initiated during the primary stage of creep, as shown (40) by tensile testing at room temperature after the various stages of creep had been arrived at. A sharp decrease in plasticity was observed in material which had just entered the secondary creep stage. Although cavities were not observable when the creep test



had been interrupted after the primary stage, room temperature tensile testing revealed the presence of micro-pores at or near to the grain boundaries. If appreciable secondary creep had occurred small defects were visible even before tensile testing.

Attempts to improve the ductility of beryllium have usually involved the production of highly pure metal, but above 100 impure beryllium can be rendered more ductile than the pure material (41) by lengthy solution treatment of extruded ingot material at 780°, followed by slow cooling to room temperature over 120 h. The improvements probably result from the selective precipitation of some impurity round the grain boundaries.

The observation of Christy (42) that the activation energies for both creep and diffusion (43) are greatly increased by hydrostatic pressure can be explained in terms of the volume increase due to the defects responsible for diffusion, and offers additional evidence in favour of the well-established dislocation climb mechanism. Bystrov *et al.* (44) concluded that the activation energy associated with steady state creep was equal to the sum of the energies for self diffusion and for the formation of excess vacancies, although the true relationship between creep and diffusion is still unfortunately rather obscure. While Lee & Maddin (45) found that torsional deformation increased self-diffusion rates in single crystals of silver by factors as large as 100, other investigators (46) have been able to detect little or no increase in the rate during conditions of tensile or compressive strain. Similar conclusions were arrived at by Christy (42), who calculated that the theoretical increase in vacancy concentration during deformation was smaller by several orders of magnitude than that which could be needed to account for some of the increased diffusion rates reported.

A pronounced increase in creep rate occurs during the process of ordering at temperatures below the critical value (47). The activation energy for creep in the ordered lattice is greater than that in the disordered lattice. These results, obtained on  $\text{Ni}_3\text{Fe}$ , support the dislocation climb mechanism, and suggest that the diffusion of vacancies associated with this process is anisotropic with regard to slip band orientation.

The influence of stress on the rate of creep in the dislocation climb range is more difficult to interpret than that of temperature, as the effect of a stress change is primarily dependent upon the substructure previously developed (48). Thus, if the applied stress is suddenly decreased, the initially high creep rate diminishes gradually as the dislocation arrays thin out by climb. An increase to the secondary creep rate appropriate to the induced stress occurs as the original dislocation barriers recover and are replaced by a more widely spaced array. The creep rate may be controlled either by the actual climb of the dislocation or by a number of micro creep mechanisms. Theoretical considerations predict that in a pure

metal the creep rate, being controlled entirely by dislocation climb, should vary as the 4.5 power of the stress (49). Because of the number of microcreep mechanisms available, an alloy is more likely to exhibit a third-power dependence. Dilute alloys of lead and indium behave in a manner which confirms these predictions (49). As the alloying content increases, the stress exponent falls from 4.5 to approximately 3. The activation energies associated with the hot deformation behaviour of pure indium and lead are those of self diffusion; at temperatures higher than 0.6 of the absolute melting point dislocation climb is the limiting process (50). Small holes such as those existing in a powder metallurgy product can, by acting as vacancy sinks, increase the rate of creep considerably (51). At fairly low temperatures, when the rate of arrival of vacancies is the slowest process, the size and efficiency of the voids is of little importance.

The experimental difficulties encountered during creep testing at temperatures above 1000° are considerable (52), and undue emphasis upon the purely technical details of this type of work frequently obscures the value of the reported data. Thus Mordyke (53) does not report on the grain size or purity level of the refractory metals he tested in spite of the sensitivity of these materials to interstitial contaminants, although in a later paper (54) on iridium of known purity he reported that above 1600° the fractures of iridium were completely transcrystalline and considerable grain boundary movement occurred.

No radically new method of deducing long-period creep and rupture properties from the results of short-term tests has yet been achieved, although considerable attention has been devoted to this problem (55-57). The Larson-Miller parameter can compensate for variations in strain rate, and permits the time-temperature function to be considered as a modified temperature (55, 57). Hot tensile, hot hardness and creep rupture data can all be neatly incorporated on to one curve by using this parameter, and the sharp discontinuity in the resultant curve demonstrates convincingly that the 'equicohesive point', which separates high- and low-temperature deformation behaviour, is invariant when strain rate effects are accounted for (55).

Although these results are of practical rather than theoretical importance, it is perhaps significant that the most effective methods of correlating time and temperature effects are based upon the Arrhenius rate equation. Conrad (56) has demonstrated that the successful Manson-Haferd parameter, usually considered as an empirical function, represents a special form of a rupture equation developed on the basis of high temperature deformation as a diffusion-controlled process. The activation energy associated with the failure of Nimonic 90 is approximately equal to that for the self-diffusion of nickel or cobalt, while that of Nimonic 80A may

possibly be equated with the diffusion of aluminium within this alloy.

Structural changes which result in density changes can more than compensate for certain low creep rates. Fountain & Karchinsky (58) have demonstrated that the shrinkage caused by precipitation from iron-tungsten or nickel-molybdenum alloys compensates for low steady-state creep-rates in tension. In order to maintain constant strain during stress relaxation tests a gradually increasing load was required. This observation may be of practical importance in high-temperature bolting applications.

### High hydrostatic pressures

Experiments (60) on the effect of pressure on the melting-point of iron, within the range 1-96,000 atmospheres, suggest that the boundary temperature of the earth's core is  $2340 \pm 200^\circ$ . The critical shear stress also increases with pressure, being, in the case of tin, for example, nearly six times as high at 150 as at 50 tons/sq. cm. (61). At 300 tons/sq. cm., shear strengths approach that of the perfect lattice (62). The shear stress-strain curve of brittle cast iron rises considerably as the pressure increases except for a discontinuity in the pressure dependence between 24 and 35 tons/sq. in. Above this discontinuity cast iron behaves as a ductile material (63). The flow stress increases with pressure in all recorded instances with the exception of single crystals of nickel (64), but the increase is larger than that predicted from the change in shear modulus with pressure. The existence of a linear dependence between true strain and pressure has been demonstrated by tensile tests on duralumin, iron, and various steels at pressures up to 29,000 atmospheres (65). While this linear dependence is not confirmed by other workers there is no doubt that the true strain to failure is enormously increased by hydrostatic pressure. The work hardening resulting from hydrostatically induced plastic deformation is more uniform than that existing in mechanically strained specimens, which is partly attributable to minimised surface friction effects (66). Single and polycrystalline metal and alloy specimens *work-harden more rapidly under hydrostatic pressure than under simple mechanical straining* (64, 67), and improved mechanical properties at atmospheric pressure can be achieved. Hydrostatic pressure has no effect upon deformation twinning in zinc, the incidence of which is determined purely by the operative shear stress (64).

To achieve reproducible high-pressure test results the surface of brittle specimens must be protected with an impermeable film of rubber or Neoprene (63), since under high pressure fluid penetrates into the incipient surface cracks of unprotected specimens and causes premature failure. The criterion of failure in brittle materials depends on the volumetric compression stress. When this is

appreciably greater than unity, failure begins at a critical value of the shear stress. For negative or small positive values of volumetric compression, failure occurs at a critical value of the maximum tensile stress (63). Inter-crystalline failure during tensile creep testing can be avoided by the application of a hydrostatic pressure greater than the applied tensile stress (68). The results obtained with copper tested at 400-500° suggest that pressure inhibits the growth of void nuclei at grain boundaries.

Current production developments involving plastic deformation reflect the practical implications of this theoretical work. Attempts are now being made, for example, to extrude brittle materials which, when handled in the normal way, are so badly cracked that the product is useless (69). By carrying out the extrusion inside a chamber which can be pressurised up to 60 tons/sq. in., billets of magnesium and bismuth can be reduced cold by a factor of 3.16 to produce rods and tubes of high surface finish. Higher fluid pressures are required to achieve satisfactory results with 60/40 brass (70). Another recent proposal to minimise the tensile stresses which cause surface cracking during extrusion adopts a rather more crude approach (71). A back pressure, exerted in a direction opposite to that of the extrusion ram movement, is applied over the whole of the cross-section of the leading end of the extruded product. Inner and outer layers of the issuing material are thereby restrained from moving at different speeds.

The logical development of such processes is true hydrostatic extrusion in which the rigid ram is replaced by a liquid under pressure (67). The metal emerges, not into the surrounding atmosphere, but into a vessel in which a high hydrostatic pressure is maintained, for which are used liquids which do not solidify and whose viscosity does not increase with pressure. The transition from static to dynamic extrusion conditions is pronounced, being accompanied by a large, sudden decrease in the pressure required. The energy stored in the high-pressure fluid accelerates the extruded metal, which leaves the die at several hundred metres per second. Extrusion pressures for pure aluminium are reduced by a factor of approximately four. This decrease is attributable to the elimination of friction between billet and container walls.

Conditions at the interface between the deforming tool and the deformed metal during working operations are receiving particular attention. Matters can be so arranged that lubricant is trapped within the tool/metal interface: the work is deformed largely by fluid pressure and matt, non-reflective surfaces are produced (72). Anomalously low coefficients of friction are measured in such processes (73). By rotating the deforming platens, thus inducing slipping at the tool/work interface, similar effects can be obtained (74). The reduced coefficients of friction ensure more uniform deformation and a reduction in the total load required.

Explosive forming, at present being investigated largely on an empirical basis (see Supplementary Bibliography) depends upon the combined effects of hydrostatic pressures and high strain rates. Deshpande & Singh have made a detailed metallographic study of slugs emanating from the cones of hollow charges fired into water (75). Differences between the extent of the deformed zone in steel and copper slugs are attributed to the differing thermal conductivities of the two materials. Copper targets attacked by shaped charges at room temperature and at  $-75^{\circ}$  do not, in contradiction to the low-temperature observations of Blewitt, exhibit any deformation twinning (76). Double-acting powder presses, activated by an explosive charge, have been used to produce metal compacts containing a ductile bonding medium (77).

### Refractory metals

The current demands of the rocket and aircraft industries provide a powerful stimulus for the development of refractory alloys. Because of the insistence upon high-temperature properties little interest is being displayed in unalloyed molybdenum, niobium, or tantalum for structural purposes, although pure tungsten is likely to be used in sheet form (78). Elevated temperature strengths decrease in the order tungsten-, molybdenum-, tantalum- and niobium-base alloys. On the basis of strength-to-weight ratio this order changes to molybdenum-, tungsten-, niobium- and tantalum-base alloys (79). Spirited competition between niobium- and molybdenum-base alloys for leading-edge applications has been reported by Jaffee *et al.* (78). Tungsten- and tantalum-base alloys are employed as forgings in rocket motors.

In spite of this empirical bias, detailed studies of the relatively pure metals have provided valuable information on the deformation and fracture of the body-centred cubic transition elements. Coarse-grained niobium with a sufficiently high interstitial impurity content has a well-defined transition temperature (79a). Johnson has shown that the tensile yield stress of fairly high-purity niobium is independent of grain size, while molybdenum displays in a pronounced manner the inverse square root dependence upon grain size predicted by Stroh (80). This result implies that dislocation locking in niobium is negligible compared with that in molybdenum. Small quantities of hydrogen, which result in strain ageing, restore some degree of grain size dependence to niobium, the effect again being attributable to dislocation locking (81).

Limitations of the powder metallurgy technique have been accentuated by the demand for large alloyed ingots, and production, with certain exceptions, is generally undertaken by vacuum arc or electron bombardment melting (78, 82-84). These cold mould processes yield ingots having large columnar grains.

Because of the low grain-boundary area available, interstitial impurities have to be reduced to levels much lower than would be tolerable in a powder metallurgy product. High-vacuum processes facilitate the attainment of this high degree of purity, which can also be achieved by small additions of rare earth elements such as cerium, yttrium and lanthanum (85, 86). Knapton, who has reported on the niobium-rhenium (87a) and niobium-zirconium systems in some detail, concludes that strain energy contributions may account for differences in the constitutional behaviour of certain tantalum and niobium alloys (87b). Haworth (88) surveys the formation of intermediate phases in alloys of the refractory transition elements, while Goldschmidt (89), who has investigated the niobium-chromium-silicon and niobium-boron-molybdenum systems, stresses the importance of miscibility gaps in solid solution diagrams as a means of obtaining age-hardening effects.

Pure niobium, although ductile and readily weldable, has mechanical properties at high temperatures inferior to those of the other refractory metals (79, 90-92). Many of the niobium alloys, which are comparable in strength to those based upon tantalum and molybdenum, forfeit much of the ductility of the pure metal (78), the two most effective strengtheners being vanadium and zirconium, which tend unfortunately to reduce high-temperature ductility (79). Because of their low transition temperatures, alloys of the general composition 60 niobium, 30 tantalum and 10% tungsten have more promising characteristics, and display an unusual combination of high room-temperature impact strengths and high tensile strength at elevated temperatures. If alloys having impact transition temperatures higher than 260° are rejected, 15% of tungsten and 4% of molybdenum represent the practicable alloying limits (78). The mechanical properties of niobium-based alloys, most of which are commercially available, have been surveyed by Lement & Perlmuter (79). Titanium improves the workability and oxidation resistance but reduces high-temperature mechanical properties. This tendency is compensated for by the use of relatively large quantities of tungsten (91).

Although niobium has a low neutron cross-section, heavy irradiation results in greatly reduced ductility (92). A flux of  $10^{20}$  neutrons per sq. cm. reduced the elongation of material tested by Makin & Minter (93) from 17 to 2%. Annealing restored the discontinuous yield point. The same activation energy, 1.0 eV, is associated with the recovery process over the temperature range 80-120° of both plastically deformed and neutron-irradiated niobium (80).

High-purity tantalum can be produced by thermal decomposition of the iodide (94) or by vacuum-arc melting material to which suitable quantities of carbon have been added (95). The purity of zone-melted tantalum is faithfully reflected in its room-temperature

electrical resistivity (96), although hardness testing offers a simpler and more sensitive indication of interstitial impurity content (97).

Although 0.1% of carbon improves considerably the high-temperature properties of tantalum, the most effective method of strengthening is by the addition of relatively large quantities of tungsten, hafnium, niobium or vanadium, all of which go into solid solution (79). A practicable working limit for electron-beam melted material is 15% of tungsten (82). Small additions of titanium and zirconium in conjunction with carbon (79) provide significant dispersion-hardening effects in these alloys.

There is unanimous agreement that deformation and neutron-irradiation produce the same type of defect in tungsten (98). Over the temperature range 300–450° an activation energy of 1.7 eV is associated with the annihilation of the vacancies so produced. Single crystals of tungsten produced by floating zone refinement can be strained appreciably at room temperature without failure (99). Between 77° and 20°K plastic deformation occurs by slip or by twinning on {112} planes. Room-temperature deformation is confined to <111> directions on either {111} or {112} planes (99). Transmission electron-microscopy confirms that the principal characteristics which ductile specimens of tungsten have in common is an absence of grain boundaries (100). Although low angle boundaries do not cause brittleness, polygonised material fails by cleavage (101), and it seems probable that fracture in sufficiently pure tungsten occurs by cleavage, but is initiated at a grain boundary, the inference being that precipitates act as stress concentrators. Leber (102) used a modification of the Berg-Barrett double crystal X-ray diffraction technique to analyse the lattice plane distortions of an arc-cast tungsten grain. Distortions (in specimens of purity not given) were due to the combined effects of subgrain formation and lattice curvature. The complex sub-boundaries contained varying proportions of edge and screw type dislocations.

Braun & Sedlatschek's (103) survey of solid-state deoxidants casts doubt on the assumption that the brittleness of tungsten is due primarily to grain-boundary oxide precipitation. Although boron deoxidised the metal to a very high degree, no relationship between oxygen and mechanical properties could be established. Thoria was the most effective of the refractory oxide additions, but zirconia was rather easily reduced by tungsten at high temperatures.

Very pure tungsten can be obtained by arc melting in vacuum, or under a low pressure of hydrogen (83). This material can be extruded at 1650° and subsequently hot forged and rolled. Oxygen, nitrogen and hydrogen contents are all less than 1 p.p.m. and the recrystallisation temperature is in consequence very low. Although

traces of impurities have long been known to increase the recrystallisation temperature of tungsten, the optimum results are not obtained unless certain combinations are present (104), thus suggesting that a discrete compound phase is responsible for the improvement. Neimark & Swalin's recent study (98b) suggests that the low-temperature recovery of tungsten is primarily influenced by dissolved interstitial impurities rather than a discrete phase. It is unlikely that recrystallisation and low-temperature recovery are controlled by the same factors, and a second phase must necessarily be in equilibrium with a saturated solid solution. The two mechanisms proposed are therefore by no means contradictory.

Relatively pure tungsten will resist stresses of about 1000 p.s.i. for 200 minutes at 2800° and about 4000 p.s.i. for the same time at 2250° (105). Ductility is reasonable, failure in tension occurring by intergranular fracture over this temperature range. Between 980 and 1205 greater ductility has been reported by Pugh (106). Recent surveys by Tietz (107) and Austin (108) emphasise the lack of data on tungsten alloys and the effect of specific alloying additions upon the ductile-brittle transition temperature. Of the alloys so far evaluated, that containing 0.9% of niobium and 0.1% of zirconium appears most promising (79). It is not known whether the improvement is due to solid solution or dispersion hardening.

The ductility of molybdenum at room and lower temperatures is profoundly influenced by its carbon content. Refinement by the floating zone technique has shown that the 5 ft.-lb. transition temperatures range from -180° with 0.001% carbon to -40° with 0.008% carbon. Slight notching increased the transition temperature of the 0.001% carbon crystals to 230° (109). As the lowest impact transition temperature for normal notched polycrystalline molybdenum is 350°, even this result is encouraging. Carbon is intentionally added to remove oxygen during arc melting, but the alternative use of lanthanum and yttrium has been suggested (86). These rare-earth metals have a high affinity for oxygen and are virtually insoluble in molybdenum, any slight excess being readily removed by zone refining. The transition temperature of recrystallised molybdenum is always well defined, but progressive cold working extends the transition over an increasing temperature range. Heavily cold-worked molybdenum sheet is, therefore, relatively ductile (110). Fracture at temperatures well above the transition temperature appears to be due to the joining of many cracks which grow co-operatively in a narrow band across the specimen. Grain boundaries are sufficient to prevent crack propagation, the final stage of fracture being one of shearing at or near the grain boundaries (111).

Although detrimental at low temperatures, carbide dispersions can considerably improve the high-temperature properties of



molybdenum alloys (112), while optimum effects are achieved in alloys containing small additions of titanium or zirconium. Sufficient titanium must be present for the formation of titanium carbide rather than molybdenum carbide, which is much less stable, and massive particles of it result in diminished creep properties.

It is unlikely that pure molybdenum will be used for structural purposes. Alloys containing approximately 0.5% of titanium are approximately twice as strong as pure molybdenum between 900° and 1200° (78, 113), and zirconium additions are similarly effective (114). Neither the pure metal nor the alloys provide ductile fusion welds.

The most effective method of obtaining ductile tungsten and molybdenum is to alloy with rhenium (115). Cast molybdenum alloys containing 33-38 at.-% of rhenium can be cold worked at room temperature. The boundary of good workability at 1200° extends from 21 to 42 at.-% of rhenium. Tungsten alloyed with 23-32 at.-% of rhenium can be readily worked at 1000°, while the workable range at 1400° extends from 18-33 at.-% of rhenium.

The addition of 50%, by weight of rhenium reduces the transition temperature of recrystallised molybdenum from room temperature to below liquid-hydrogen temperature (116). The transition temperature of recrystallised tungsten is similarly reduced from 330° to room temperature, as the rhenium content increases to approximately 27%, the limit of solubility at 2500° (117). A further increase of rhenium content to 30% eliminates all the benefits achieved by raising the transition temperature to 250°. Jaffee *et al.* (118) attribute these improved properties to a combination of circumstances. Thus the complex molybdenum rhenium oxide formed does not wet the grain boundaries like the familiar molybdenum dioxide grain-boundary eutectic and its extreme volatility promotes a general decrease in oxygen content. The improved low-temperature ductility is largely due, however, to the elimination of dissolved interstitial impurities. This effect, demonstrated by the pronounced decrease in cast hardness achieved by alloying molybdenum, tungsten and chromium with 5 at.-% of rhenium (115), can be interpreted in terms of Robins' hypothesis (1), which predicts reduced interstitial solubilities in Group VIA metals as elements of higher groups are added.

The serrated stress-strain curves displayed by these alloys are due to twinning rather than to interstitial effects. Rhenium promotes deformation twinning, and Feng (119) reports that rhenium-molybdenum alloys twin consistently on {112} planes over a wide range of alloying compositions. The plastic strain at which twinning commences is inversely proportional to the amount of rhenium in solid solution.

Savitskiĭ *et al.* (120) provide important data on the high-temperature properties of rhenium-tungsten alloys produced by powder metallurgy. The electrical resistivity of tungsten at various temperatures is increased several times by the addition of rhenium, and the ductile alloys will undoubtedly find wide electrical engineering applications.

In accordance with Robins' hypothesis the platinum group metals also appear to reduce the interstitial content of the refractory transition elements. By reducing the oxygen content of molybdenum to a level estimated at 5 p.p.m., additions of 0.1 at.-% of most of the platinum metals appreciably lower the cast hardness of the metal (121). Larger additions of ruthenium, osmium and platinum promote room-temperature deformation twinning in molybdenum, tungsten and chromium, although these alloys have, unfortunately, higher transition temperatures than those of unalloyed molybdenum. Additions of ruthenium and further binary additions of iridium or palladium do, however, decrease the bend transition temperature of relatively impure cast chromium (122).

Attempts to improve the ductility of the refractory platinum metals have not been particularly successful. Single crystals of rhodium, produced by floating zone refinement, can be reduced cold by approximately 90% in cross-sectional area (123) and subsequent annealing produces a brittle polycrystalline wire. Vacuum fusion analysis by Allred *et al.* (124) show that zone refining reduces the oxygen contents of ruthenium, platinum and rhodium to 7, <1 and <2 p.p.m. respectively, and these values can be correlated with the relative ductilities. Although these workers report improved ductility in zone-refined ruthenium, Rhys found that zone-refined iridium or ruthenium could not be cold worked (125).

The purity of rhenium, according to Churchman, has little effect upon its ductility (126), the high rate of work hardening being associated with the barriers formed by interacting prismatic slip. The cracking observed, which was intercrystalline and not cleavage, occurred when relative slip between grains was not possible. A temperature of 2500° is required to achieve complete recrystallisation in pure rhenium.

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## CORROSION

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IS a subject of such complexity as corrosion, research at a fundamental level seems to be a necessary method of attack. A deeper understanding of the mechanism of corrosion should eventually lead to more spectacular advances in methods of prevention. For this reason much of the contents of this chapter describes fundamental work which should bear fruit in the near future.

### Immersed corrosion, passivity and inhibition

The use of anodic passivation has been recommended as a practical means of controlling corrosion of steel in the chemical industry (1, 2). In laboratory studies an anodic passivation system with a high current capacity has been shown to be capable of protecting stainless steel and mild steel equipment used in contact with oxy-acids, caustic alkalis, aluminium sulphate and ammonium nitrate, although such protection is not possible in solutions containing halogen acids or salts. It is claimed that laboratory studies can be extrapolated with reasonable confidence to field performance. The method, using a newly developed automatic potential controller, has been successfully applied in a sulphonation plant (3). A manually controlled passivation method had earlier been used with satisfactory results in alkaline digesters in the paper pulp industry (4).

It has been suggested that the inhibition of corrosion of steel in neutral solution is initiated by adsorption of inhibitive anions at potentials above the zero-charge potential of the metal (5), and support for this has been gained from the action of sodium benzoate on steel rusting in NaCl solutions. The addition of the benzoate leads to inhibition (5) only at potentials above a certain critical value regarded by some workers as being that of oxide formation (6); further work is clearly needed.

### Underground and microbiological corrosion

From a study of polarisation curves for mild steel in pure cultures of sulphate-reducing bacteria, it has been shown (7) that the mechanism of microbiological corrosion originally proposed by von Wolzogen Kühr & van der Vlugt (8), that is, cathodic depolarisation brought about by the metabolism of the organism, can occur provided that the organism has an enzyme system capable of utilising elementary hydrogen. In the presence of sulphate-reducing organisms without such a hydrogenase system (e.g., *Desulphovibrio orientis*) corrosion may be stimulated only by virtue of the effect at the anode of the hydrogen sulphide generated by the activity of the bacteria.

An analysis of data (9a) from more than 150 bell-holes showed that moisture was present in greater amounts in the bottom of back-filled pipe-line ditches than in undisturbed soil, providing adequate water for bacterial growth. The moisture content of the surrounding soil also has an important effect on the coating, coal-tar coatings taking up far less water than asphaltic coatings. Aerobic conditions and high bacterial populations adjacent to the coated pipe-lines indicated that soil bacteria were obtaining food material from the coating or wrapping materials, causing decomposition of these. In these conditions cathodic protection current requirements were higher (9b).

The sources of potential difference between buried metal and its environment have been analysed (10). It is concluded that only large-scale couples can be detected by electrical measurement. Interference currents from neighbouring cathodic protection systems and stray currents from ground return circuits must be eliminated before searching for other sources of corrosion potential.

The corrosion of iron by  $H_2S$  is of importance in relation to its corrosion in the presence of sulphate-reducing bacteria. It has been shown (11) that the rate of reaction of iron and  $H_2S$  in an  $O_2$ -free system, in presence of NaCl, is controlled by the rate of diffusion of  $H_2S$  to the metal; this rate is almost unaffected by the presence of an oil-phase. In the presence of good inhibitors the corrosion rate can be reduced to a negligible value, probably because they form a particularly efficient non-permeable adsorbed film with the iron sulphide corrosion products.

Instances have been known of breakdown of asphaltic or bitumen coatings due to root penetration, with consequent corrosion at these points on the underlying iron pipe due to bacterial action. It is of interest, therefore, to note that a search has been made for suitable poisons, to be incorporated into wool-felt servings, to prevent root penetration of the coating, triethyltin oxide being the most promising (12).

### Cathodic protection

Cathodic protection is now established as a successful method of corrosion prevention. Trends in its development are mainly towards more varied and efficient types of anode (for impressed current) and towards a widening of the field of application; platinum anodes (13), silver-lead alloy anodes (14), and tantalum-platinum and titanium-platinum bi-electrodes (15) have been recommended. In laboratory tests, cathodic protection has proved of value in preventing cavitation damage on steel, stainless steel and copper (16). It was shown that protection could be obtained both anodically and cathodically provided that the voltage and current were sufficient to liberate gas at the metal surface. This protection is possibly due to the cushioning effect of the electrolytically liberated gas. Some success has been achieved in the cathodic protection of pre-stressed concrete pipe (17), always considered to be a difficult problem. A combined method of application of cathodic protection and anti-fouling measures has been devised (18). It is somewhat surprising to note a claim for the prevention of atmospheric corrosion by cathodic protection (19); tests were made in a high humidity chamber using a modified cathodic protection method and a self-conducting paint as a medium of current transfer.

### Stress-corrosion and cracking

There is increased interest in the theoretical and practical aspects of stress-corrosion (20). Emphasis is placed (21) on: (1) the relationship between stress and chemical reactivity; (2) the concept of embrittlement by localised corrosion; (3) interactions between the initiation and propagation stages of cracking and the influence of crystallography; (4) the effect of specific alloy compositions and chemical environment on failure mechanisms; (5) the application of dislocation movement to crack growth.

Studies of stress-corrosion cracking of austenitic stainless steel (22) have shown that, after an initiation period, during which partial passivation but no cracking occurred, local anodes corroded along certain narrow planes, resulting in cracking and ultimate failure. Cracks in austenitic stainless steels and magnesium-base alloys extended slowly and gradually, but in mild steel in hot nitrate solution crack propagation took place in alternating steps of rapid and slow penetration. The cracking of aluminium 4% copper and aluminium 1% magnesium alloys consisted of alternating stages of electrochemical corrosion and sudden physical failure. A novel feature of this work was the use of acoustic recording, employing a standard record-playing arm with the stylus in direct contact with the test piece, the amplified signal being transferred to a tape-recorder or loudspeaker.

The resistance to cracking of austenitic stainless steels in strong magnesium chloride solution was found to increase with both nickel and silicon content but was generally unaffected by carbon, nitrogen, manganese, and chromium contents within commercial limits (23). The negligible effect of the carbon content (between 0.014 and 0.1%) has been confirmed by other workers (24). Variations in heat treatment and surface conditions were relatively ineffective in changing the cracking times but treatments designed to apply an oxide film produced some improvement in the resistance to cracking.

The behaviour of niobium-stabilised austenitic stainless steel has been examined at various stresses in chloride and caustic solutions of concentrations ranging from 100 p.p.m. to 75%, and at temperatures up to over 300°C (25). The rate of stress corrosion attack was dependent upon all these variables. Attack by alkali hydroxides can be either inter- or trans-crystalline, depending on conditions of test. Additions of sodium phosphate or nitrite greatly reduced the rate of attack under all conditions of test, and it is possible that such additions may be effective under some operating conditions.

Electron microscopy and diffraction techniques have enabled a correlation to be made between microstructure and stress-corrosion-fracture behaviour of hardened 12% chromium steels (26). When tempered at 650°F these steels cracked at low stresses along networks of essentially untempered martensite in the prior austenite grain boundaries. Tempering at 1175°F broke up the continuous martensite network and reduced stress-corrosion susceptibility but also reduced tensile strength.

Tests on mild steel in caustic soda and nitrate solutions showed that grain-boundary corrosion predominated at long extensive stresses while at low stresses localised corrosion predominated, indicating the interchangeability of these two types of phenomenon (27).

Screening tests for materials for nuclear power plants have been described (28). Stressed U-bend specimens were exposed in a tilting autoclave to both liquid and vapour phases of a synthetic boiler water solution of high pH, containing oxygen, phosphate and 500 p.p.m. of chloride ions. Stainless steels with low carbon and nitrogen content were more resistant than niobium-stabilised 18-8 stainless, while Inconel, monel, nickel and titanium were completely resistant. Ferritic steels were crack-resistant but suffered pitting attack. Tests on a number of high-alloy steels and high-nickel alloys under conditions simulating those in a pressurised-water nuclear power plant, showed the high-nickel alloys to be the most resistant (29).

The influence of protective coatings, stress level and tempering temperature on the atmospheric stress-corrosion of steels for aircraft and missiles has been examined (30). Tempering at 1100°F or

higher, and the use of protective coatings that are anodic to steel, can improve the resistance of very high-strength alloys.

In an examination of the influence of polarisation on the nature of corrosion cracks in brass (31), it was found that insufficient cathodic polarisation increased the time to cracking. The cracks had blunted ends and tended to expand laterally across the grains, but on anodic polarisation the cracks were even narrower than in the absence of polarisation and the narrow slits at their ends were elongated.

The stress-corrosion behaviour of an aluminium-7% magnesium alloy has been investigated to ascertain which types of grain-boundary are sensitive to corrosion (32). Large-angle grain-boundaries, normal to the tensile stress, are particularly liable to be attacked. Where heterogeneous efflorescence occurs, these are particularly prone to fissurise, and represent the initial intercrystalline condition for subsequent intercrystalline stress-corrosion phenomena.

The influence of metal ions in the corroding agent, particularly those of copper in trace amounts, on the stress- and intercrystalline-corrosion of aluminium-7% magnesium and aluminium-copper-magnesium alloys has been examined (33). With both alloys, both types of corrosion increased when the metal ions in the corrosive medium had a more noble normal potential than that of the alloy. The preferential attack along stacking faults arising during the electropolishing of copper alloys is considered to be related to the formation of cracks in these alloys in corrosive media (34).

A Perspex crack-model has been devised to investigate the movement of electrolyte into thin cracks (35). It has been shown (36) how a duplex specimen, consisting of a layer of susceptible material on the test material may be used to determine the tendency to stress-corrosion-cracking of the second material. In the case of nickel and stainless steel the cracks in the latter stop at the nickel boundary.

### Corrosion in nuclear technology

In the design of nuclear reactors and of their immediately associated equipment many novel corrosion problems arise, since materials are selected by criteria not applying in other industries. Only a few metals qualify as nuclear fuels and, without alloying or other protective measures, their corrosion resistance is generally not good. They are contained in alloys of low neutron absorption. The gas or liquid surrounding the sheathed fuel must often, in addition to having acceptable corrosion properties, act as a moderator, heat transfer medium or both. The effect of irradiation on the corrosion products is sometimes more important than any loss of metal by corrosion.

From the corrosion viewpoint reactors may be divided into

those cooled and moderated by gases and those in which water fulfils these functions. The corrosion problems of water-cooled reactors were considered at a recent conference (37). Draley discussed the resistance of uranium alloys to high-temperature water. The most useful alloy, containing 5% by wt. of zirconium and 1½% niobium, is most resistant in the quenched condition, although it is then susceptible to irradiation damage. Draley regarded the hydrogen developed during corrosion as the prime agent in film breakdown, but Waber (37), while allowing that 'hydrogen damage' plays some part in the corrosion of uranium alloys, considered that the stresses built up in the oxide film also have an important effect.

Among fuel cladding materials zirconium and its alloys have continued to occupy much attention. Cox (37) described an investigation by electron microscope which showed that the 'transition' in oxidation kinetics was accompanied by the formation of cracks in the oxide film. The formation of cracks had also been inferred (38) from capacity measurements, which showed that steam oxidation can produce more pronounced cracking than exposure to oxygen. Interest has recently moved to temperatures rather higher than those of pressurised water reactors, as exemplified by the study of Pemsler (37), which extended to 540°. At such temperatures, alloys of the Zircaloy type are no longer the most resistant: Pemsler's most successful alloy contained nickel 0.6% and chromium 0.3% by wt.

It is well known that part of the hydrogen liberated during corrosion enters zirconium and its alloys, in which it is soluble. The possibility of this affecting the mechanical properties has stimulated work on corrosion-induced hydrogen uptake. The subject is reviewed by Bieffer *et al.* (39). Attempts have been made (40), by alloying with known catalytic poisons, to reduce the hydrogen uptake by corroding Zircaloy 2. Additions of arsenic, antimony, bismuth and tellurium were ineffective; but Berry (37) showed that when the nickel content of the alloy was reduced from the normal 0.03% to 0.002% by wt. there was a reduction in uptake.

The usual structural material for high-temperature water circuits is austenitic stainless steel which, although satisfactory in very pure 'primary' water, has sometimes suffered stress-corrosion cracking in the less-pure water of the secondary part of the circuit. Possible alternative materials are reviewed (41). Though free from stress-corrosion, carbon steel, nickel, monel and 2½% chromium steel were ruled out because of pitting or crevice corrosion. A 16% chromium steel was considered and Inconel was chosen as the best alternative to austenitic stainless steel. However, although White (41) found Inconel not subject to stress-corrosion cracking, Coriou *et al.* (38) reported that alloys of this type did suffer intergranular stress-corrosion in high-temperature water.

Corrosion products of structural materials, suspended in the water, are important because of deposit formation and the carrying of induced radioactivity to all parts of the circuit. Recent observations from reactor systems are summarised by Breden (37).

Carbon dioxide is the coolant in many gas-cooled reactors. The resistance of a number of structural materials to this gas has been studied between 600° and 950° (42). Although some stainless steels had sufficiently low overall weight gains, they were subject to localised or intergranular attack. Materials acceptable by oxidation (and other) criteria included Type 316 stainless steel and Inconel.

The low cross-section of beryllium suggests its use for fuel cladding, stimulating interest in its oxidation resistance. Jepson *et al.* (43) studied beryllium in dry oxygen and in CO<sub>2</sub>-CO mixtures. In the former, 'breakaway', with formation of a non-protective film, was first found at 750°. At 500°-600° oxidation rates decreased continuously up to 300 hours' exposure.

### Atmospheric corrosion of steel

Until recently most studies of the chemical processes occurring in atmospheric corrosion have been devoted to the initiation and early stages of attack. These have an important bearing on the storage and transportation of metallic goods, but are of little significance to the maintenance engineer. Some recent papers and discussion remarks have dealt with the more advanced stages of rusting of steel. It has, for instance, been discovered that there is a significant seasonal variation in the ferrous sulphate content of rust formed on steel exposed to an urban atmosphere, at Cambridge, England (44), the salt being mainly located in the adherent rust next to the metal. Paint coatings based on a red-lead linseed-oil primer were found to break down more rapidly when applied to this rusting steel in winter than when applied in summer. Mechanical treatment of the surface to shatter the rust, followed by washing, should improve the performance of the subsequently applied paint.

The painting of rusty steel has recently been discussed (45a) but Hudson (45b) considered the proposal to be premature. Nevertheless, a study of rust constituents should be useful. Harrison (45c) described experiments in which steel panels were treated with aqueous solutions and allowed to rust before painting. Ammonium sulphate was found to shorten the life of the paint film more than any other reagent, including sulphuric acid, and it was suggested that the ammonium ion adds significantly to the corrosive effect of atmospheric sulphur pollution. In earlier corrosion tests (46) it has seemed that, with certain exceptions, there is a limiting sulphur pollution content above which very little increase in corrosion rate is produced. The main exception was at Billingham, where the

sulphur pollution and corrosion rate were both very high; the high ammonia content of the atmosphere may account for this apparent anomaly (47).

The derivation of simple relationships between rate of atmospheric corrosion and environmental conditions is complicated by the large number of variables. By plotting the amount of corrosion on a scale determined by a defined 'time of wetness', Sereda (48) has detected a dual dependence on sulphur pollution and temperature. Russian workers (49) have shown that corrosion of steel stops entirely at temperatures well below zero, but their claim that this discovery refutes certain statements by Vernon (50) is unsound; the Russian winter may halt corrosion, but in England the increased pollution and humidity during the winter more than offset the effect of the smaller fall in temperature.

An analogy has been drawn between the influence of water vapour on the oxidation of iron at 450° and the concept of 'critical humidity' in atmospheric corrosion at ordinary temperatures (51). Reaction between zone-refined iron and dry air for 48 hours at 450° led to the growth of 'whiskers' on the normal oxide film. If 3% water vapour were added to the oxygen, the same oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) grew in the form of platelets which were far more bulky than the oxide whiskers. It was suggested that 'hydrogen atoms or ions from the water vapour act to enlarge the area for reaction'. Arguing from analogy, the authors suggest that the influences introduced by water vapour at high temperatures may also play a part in ordinary atmospheric corrosion. Unfortunately, the suggestion has been described in some technical journals as a 'new theory of atmospheric corrosion'. It is therefore proper to suggest that, whereas the atmospheric corrosion of iron at 'super-critical' humidities is essentially an electrochemical process, the high-temperature reaction is a surface reaction with diffusion of ions in a solid lattice. If hydrogen ions in the oxide lattice play any part in atmospheric corrosion, it will probably be extremely difficult to detect.

### Surface treatment and protective coatings

A process is described for the preparation of cleaned steel surfaces for painting (52), in which a metal salt solution is applied and reacts to form insoluble metal compounds. By subsequent flame-scarfing the thin film of metal compounds is burnt into the surface of the steel and forms a continuous, very thin, amorphous protective layer.

A new type of coating, 'Galvalloy', is stated (53) to consist of two finely divided metals incorporated into a plastic medium. After application, the metals separate into two layers, the lower affording galvanic protection to the steel, while the upper,



presumably in leaf form, protects the functional coating from atmospheric oxidation.

The resistance of niobium to oxidation at high temperatures is improved by a new two-stage coating process (54). The niobium is dipped into molten zinc, and is then annealed in air at 870° to induce the alloying of the two metals and to produce a resistant mixed oxide layer. Outdoor and laboratory corrosion tests (55) have confirmed that improved protection is given to steel and zinc-based die-castings by plating with layers of chromium-nickel chromium or copper-chromium nickel chromium as compared with nickel-chromium or copper-nickel chromium deposits. The improvement is due to the action of the lower layer of chromium in diverting pits laterally into the Ni instead of allowing downward penetration into the basis metal. A method (56) has been developed for electrodepositing an iron-chromium-nickel alloy, corresponding to 18-8 chrome-nickel steel, directly from an aqueous solution of the three sulphates, urea and boric acid. By an appropriate choice of concentrations, pH, and temperature, the deposition potentials of the three metals and the alloy are brought to the same value of  $E_H = -0.68$  V. The process is sensitive to changes in concentration of the various bath constituents, however, and deposition is influenced and limited by the formation of a diaphragm of chromium hydroxide.

### Corrosion: friend or foe?

In an article on the economics of corrosion, it has been pointed out (57) that corrosion prevention does not always 'pay'. This is because corrosion prevention does not increase revenue, but lowers costs—unattractive in periods of high taxation when maintenance is directly deductible against tax.

Actiography, etiography, or ethiography is the name given to the study of the destruction of solid bodies by rapid or slow, mechanical or chemical means (58). Amongst these, corrosion plays its part. This study is now being developed into a new art-form, and considerable attention is being given, by at least one enthusiast, to finding ways of controlling this disintegration of solid materials so as to produce forms of artistic merit after desired intervals of time.

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# ORGANIC CHEMISTRY



## HEAVY ORGANIC CHEMICALS

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### Acetylene

THE first plant to use the Société Belge de l'Azote (S.B.A.) acetylene process on a commercial scale was brought on stream early in 1960 at the Carling works of the Houillères du Bassin de Lorraine. In the process, methane, obtained as a by-product from ammonia synthesis, and oxygen are separately preheated to 600°, mixed, burnt, and then shock-cooled by passage through a curtain of water. Both the burner and combustion chamber are made wholly of metal. The acetylene finally obtained has a purity of 99.4% (1).

### Acids and anhydrides

Pimelic acid is now being manufactured in market development quantities by American Cyanamid of New York, and its use is being studied in the development of novel polyester and polyamide resins and films. Pimelic esters may also prove to be useful plasticisers for polyvinyl chloride (2).

A recent Russian development is the manufacture of aromatic dicarboxylic acids or diamines from alkylbenzenes, ammonia and oxygen with catalysts such as oxides of vanadium with titanium or tin additives. The oxidative ammonolysis reaction gives rise initially to dinitriles, which can then be either saponified to the corresponding dicarboxylic acid or reduced to diamines; e.g., terephthalic acid can be obtained from *p*-xylene or even from certain terpenes (3).

An important innovation in phthalic anhydride process technology was the introduction, by Scientific Designs Co. Inc., of a new catalyst which allows oxidation of either naphthalene or *o*-xylene, or mixtures of the two, to phthalic anhydride in fixed-bed vapour-phase reactors. Although it has previously been possible to use *o*-xylene in plants with the normal naphthalene oxidation catalysts, lower yields have always been obtained, but with the S.D. catalyst high yields are obtained regardless of which feedstock is used (4).

Another process developed by the same company enables fumaric acid to be manufactured from almost any maleic-containing feedstock. The base material may be either pure maleic acid prepared

from benzene or butenes, or impure by-product maleic acid solutions of the type obtained in phthalic anhydride manufacture. The type of catalyst used has not been disclosed, but it is claimed that the process is a simple one which remains economically attractive even when operated at a rate as low as 1000 tons/year (5).

Peracetic acid entered the ranks of heavy organic chemicals with the starting up of Union Carbide's 10 million lb./year plant for the production of this material. In the process used, acetaldehyde is oxidised to its monoperoacetate, in the presence of ethyl acetate, by air containing ozone as a catalyst. The monoperoacetate is subjected to pyrolysis whereby free peracetic acid and acetaldehyde are obtained, the latter being recycled. The peracetic acid is used wholly by the producing company for further working up into a series of epoxy compounds, of which the most important group is epoxidised oils and fats for use as vinyl plasticisers (6, 7). Another peracetic acid process developed in the U.S.A. involves the oxidation of acetic acid with hydrogen peroxide as oxidant and a sulphonic acid cation-exchange resin as catalyst (8).

The Distillers Co. is constructing a plant for the manufacture of acetic acid by a novel process involving the direct oxidation of a light petroleum fraction. The process allows the use of a fairly wide range of light hydrocarbon feedstocks and, since only one stage is involved, it should show attractive economies over the two-stage ethyl alcohol-acetaldehyde route currently employed (9).

At the works of Farbwerke Hoechst a plant is on stream using a new process for making sorbic acid from ketene and crotonaldehyde, which are converted to an intermediate polymeric ester with a neutral zinc catalyst. This ester yields sorbic acid which is purified by a new distillation process. Both starting materials are produced from acetaldehyde (10).

An experimental plant for the production of terephthalic acid from toluene has been started up in Germany, using a method which entails the chloromethylation of toluene and oxidation of the resultant compound to terephthalic acid. The process is continuous. Dimethylphthalic acid and pyromellitic acid are to be produced from xylene in the same plant (11).

### Alcohols and esters

A range of fluorine-containing alcohols has recently been introduced by E. I. Du Pont de Nemours. These consist of a series of trihydrofluoroalcohols containing an odd number of carbon atoms (from  $C_3$  to  $C_{11}$ ) prepared by the free-radical telomerisation of tetrafluoroethylene with methyl alcohol (12).

The first petroleum-derived fatty alcohols will become available early in 1961 when the Continental Oil Co. brings on stream its

50 million lb./year plant for the manufacture of straight-chain primary alcohols. The process is based on the work of Ziegler and others (13, 14) and utilises the growth reaction of triethylaluminum with ethylene to form a mixture of higher molecular weight trialkylaluminiums. These are progressively oxidised by small amounts of oxygen (air) to mono-, di- and finally tri-alkoxides. Hydrolysis of the aluminium alkoxide mixture gives a range of straight-chain alcohols with an even number of carbon atoms. A typical reaction product contains between 15% and 20% of each of the  $C_6$ ,  $C_8$ ,  $C_{10}$ ,  $C_{12}$  and  $C_{14}$  alcohols (15).

The Celanese Corp. of America is constructing a 25 million lb./year plant for the manufacture of 1,3-butylene glycol, which has not previously been manufactured on a commercial scale (16).

#### Aldehydes and ketones

The production of formaldehyde on a large scale by the direct catalytic oxidation of methanol over metal oxides is reported by Montecatini. In contrast to the normal formaldehyde process in which the combined oxidation and dehydration of methanol is carried out with a deficiency of air in the presence of metallic (mainly silver) catalysts, the Montecatini process starts with an air-methanol mixture, with a methanol concentration below the lower explosive level. This is passed over a metal oxide catalyst at 300-400°, the formaldehyde yield being greater than 90%. Small quantities of by-product carbon monoxide and carbon dioxide are also formed. The advantages of this process are: longer catalyst life, higher yield and direct production of almost methanol-free formaldehyde solution (which obviates the need for rectification), higher reaction heat and better heat utilisation, simple and cheaper absorption equipment and reduced risk of explosion (17, 18).

The commercial production of methyl isopentyl ketone has been started by Union Carbide Chemicals U.S.A. It is claimed that this is the most economical high-boiling solvent available for vinyl and nitrocellulose lacquers (19).

#### Aromatics

As a result of the naphthalene shortage in the U.S.A., three oil companies, Sun, Ashland and Tidewater, have either planned or commenced construction of petroleum naphthalene plants, with a total capacity of 350 million lb./year, at least one of which will come on stream in 1961. In addition, new plants under construction will raise U.S. *o*-xylene capacity to 400,000 lb./year, most of which is destined for export to foreign phthalic anhydride manufacturers (20).

Apart from mixed xylenes produced by Shell, significant quantities of petroleum-derived aromatic hydrocarbons have not, so far,



been manufactured in the U.K., but two new plants are being developed. The B.P. California plant will produce *o*- and *p*-xylene and ethylbenzene (21) and a British Celanese plant will produce benzene, toluene and xylenes (22). That the demand for chemical-grade benzene is increasing rapidly in the U.K. is apparent from the fact that in 1959 the production of pure benzene exceeded that of motor benzole for the first time (23).

### Halogen compounds

A two-step process has been developed for the production of hexachlorobenzene from a partially chlorinated benzene, such as dichlorobenzene, which is treated with excess chlorine in the liquid phase to give a more highly chlorinated product. This is then vaporised and treated with excess chlorine in the presence of activated carbon, to give practically pure hexachlorobenzene.

Another development is the chlorination of hydrocarbons using hexachloroethylene and an excess of chlorine in the presence of active carbon impregnated with cupric chloride. In this way, almost pure carbon tetrachloride can be manufactured direct from methane. Also described is the preparation of tri- and perchloroethylenes (24).

### Nitrogen compounds

Glutamic acid, the monosodium salt of which is widely used in the Far East as a flavour-intensifying material, has so far been manufactured entirely from natural products. Ajinomoto Co. of Tokyo, the world's largest producer, is now constructing a plant for the synthesis of glutamic acid starting from petroleum derived acrylonitrile (25).

Caprolactam is not, at present, manufactured in the U.K., but it seems probable that large-scale production will commence in the fairly near future. British Enka and Imperial Chemical Industries (I.C.I.) have both announced plans to manufacture nylon 6, and British Celanese (subsidiary of Courtaulds) holds a nylon 6 licence. British Enka have a caprolactam process, I.C.I. are negotiating for the U.K. manufacturing rights to a Soviet process, and Courtaulds have recently purchased U.K. rights to the Snia Viscosa process. In this last-named process, toluene is oxidised to benzoic acid, which is then hydrogenated to give hexahydrobenzoic acid. The final stage is to react this with nitrosylsulphuric acid, when caprolactam is obtained directly. This process will first be used in Trieste, where a 20,000 tons/year plant is under construction (26-28).

A £3 million acrylonitrile plant, Britain's first, was commissioned by I.C.I. early in 1960 (29). The acetylene-hydrogen cyanide process used is the same as that used by the majority of acrylo-

nitrile manufacturers in other countries, although a few plants rely on the addition of hydrogen cyanide to ethylene oxide, with subsequent dehydration. Some of the newer acrylonitrile processes have, however, been developed to the commercial stage.

In Germany, Knapsack Griesheim are producing acrylonitrile via lactonitrile obtained from acetaldehyde and hydrogen cyanide (30). In the U.S.A., the Sohio Chemical Co. have a plant for a process based on ammonia, air and propylene. Basically, this is a one-step, catalytic, vapour-phase reaction carried out at moderate temperatures (below 900°F) and low pressures (less than 3 atm.) with a residence time of only a few seconds. Although the company have not given details of the catalyst, it seems probable, from a recent Belgian patent application (571,200), that bismuth phosphomolybdate is used (31, 32).

The Ugilor Co. of France are building an acrylonitrile plant which will use the Distillers Company's Ammoxidation process. In this, propylene is first oxidised to acrolein, which is then reacted with ammonia and oxygen, in the presence of a molybdc oxide catalyst, to give acrylonitrile (33).

### Paraffins and olefins

Some details of a new Shell process for the manufacture of isoprene have been revealed (34) which indicate that the cost of this important synthetic rubber intermediate should be significantly lower when new plants using the process come into operation. Starting from a mixture of butylene and isopentene, four steps are involved: (1) catalytic dehydrogenation to give a mixture of butadiene, isoprene and small quantities of other unsaturated hydrocarbons; (2) distillation to give a middle cut containing the butadiene and isoprene; (3) further distillation to separate the two diolefins; (4) final distillation to purify separately the butadiene and isoprene (35).

The required butylene is obtained by a standard butane dehydrogenation process. For the manufacture of high-purity isopentene a new extraction process has been developed in the U.S. by Sinclair Petrochemicals, which differs from the conventional process in that it enables the sulphuric acid used in the extraction to be recycled without reprocessing (36).

A Russian development described as a 'promising new method for the production of ethylene and propylene' involves the pyrolysis of ethane and propane in the presence of oxygen at atmospheric pressure and at a temperature of about 850°. Conversions of 73% of the ethane and 91% of the propane are claimed, compared with a conversion rate of less than 50% by the standard thermal pyrolysis process. The construction of a plant having a throughput of 175,000 tons/year of propane is envisaged (37).

### Phenol

The Dow Chemical Co. is putting up a 36 million lb./year phenol plant for a new process, described previously in patents (38), which is claimed to have the two great advantages over the established phenol manufacturing processes of not being dependent on benzene and of avoiding the production of excessive quantities of by-products. The process involves two-stage oxidation of toluene, first to benzoic acid, part of which is then oxidised to phenol, the unreacted benzoic acid being recycled (39). The Scientific Design Co. has also announced a new phenol process in which it claims to have overcome the problem of oxidising benzene direct to phenol with little, if any, by-product formation (40).

In the early part of 1960, the British Hydrocarbon Chemical Co. phenol plant using the Distillers cumene process was started up successfully. The plant (the first of its kind in Britain) has a capacity of 13,000 tons/year, and comprises two units, (1) for the preparation of cumene by reacting benzene with propylene, and (2) for the oxidation of the cumene to hydroperoxide, which is then split into phenol and acetone. The process is a continuous one (41).

### General

A review of radiation-induced reactions suggests that this technique could become of major importance to the heavy organic chemicals industry within the next 5-10 years. Apart from the usual chain reactions leading to polymers, various non-chain chemical syntheses such as the chlorination, sulphochlorination and sulphoxidation of hydrocarbons, and the production of compounds such as phenol, aniline and hydrazine, are described (42).

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# DYESTUFF INTERMEDIATES AND FLUORESCENT BRIGHTENING AGENTS

By

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## (1) Dyestuff intermediates

### General

THE task of the reviewer of such a field as dyestuff intermediates becomes more and more difficult as the pattern of organic chemical industry changes. Two or three decades ago almost any aromatic chemical could be regarded as being associated with the dyestuff industry; today, many such compounds have their main uses in some other field—plastics, fibres, pharmaceuticals, agricultural chemicals, etc.—and there is no question but that the bulk of patent activity is in connexion with these mainly non-dyestuff intermediates. Because these reactions are of general interest in the dyestuff intermediate field, and also for the good reason that they do not logically fall into any other section of these reviews, they are included here.

For the products required in fair tonnage, the emphasis is on continuous operation and on catalytic processes. This applies to alkylations (springing from the petroleum field), to reductions for such important products as the toluylenediamines required for polyurethanes, to oxidations (akin to the oxidation of *p*-xylene to terephthalic acid for synthetic fibres), and to catalytic isomerisations generally.

Academic studies during the period under review have been mainly concerned with physical properties such as infra-red and ultra-violet spectrum characteristics, and with kinetic studies on the reduction and sulphonation processes, and above all on the mechanism of diazotisation.

Some novel intermediates for, mainly, azo dyes are disclosed in several patents.

### Benzenoid intermediates

The various unit processes have as usual been reviewed in *Industrial & Engineering Chemistry* (1).

Friedel-Crafts alkylations of aromatic hydrocarbons with olefins

continue to receive attention; the use of an active clay or a nitro-hydrocarbon as promoter has been proposed (2), whilst enhanced yields are claimed using some oxides of metals of the vanadium group (3). Alkylation of toluene with aliphatic alcohols in presence of molecular complexes of alcohols and boron trifluoride at 50–60 atm, and 170–180° gives mainly *p*-alkyltoluenes and a small proportion of dialkyltoluenes (4).

There has been a number of investigations on the chloro-alkylation of a variety of aromatic compounds. Toluene or xylene may be chloroalkylated continuously in good yields by treatment with hydrochloric acid and formaldehyde if the aqueous hydrochloric acid is drained off periodically, cooled, saturated with hydrogen chloride and returned to the reaction mixture (5). When chlorobenzene is treated with paraformaldehyde and anhydrous zinc chloride, only *p*-chlorobenzyl chloride is formed and no *o*-isomer could be isolated (6). An acetone solution of *o*-nitrophenetole, on chloro-alkylation with dry HCl and paraformaldehyde in presence of anhydrous zinc chloride, gave 2-nitro-1-chloromethylphenetole in good yield (7); 3-nitro-1-chloromethylphenetole and 4-nitro-2-chloromethylphenetole were also prepared similarly in good yield. Arayan & Titanyan (8) have investigated the chloromethylation of phenols and cresols extensively. Good yields of the corresponding chloromethyl compounds were obtained by carrying out the reaction in benzene solution with formaldehyde and concentrated hydrochloric acid saturated with HCl gas.

Several patents have been taken out on the isomerisation of dichlorobenzenes. One describes continuous isomerisation of *o*- and *p*-dichlorobenzene in a reaction vessel fitted with a rectification column, at elevated temperature in the presence of aluminium chloride, surface-active agents and compounds of metals of the 1st, 2nd, 4th and 8th Group of the Periodic Table. A 90% conversion of *o*-dichlorobenzene to *m*-dichlorobenzene is claimed (9). Another patent describes an improved process for the preparation of *m*- from *p*-dichlorobenzene (10). Isomerisation of *o*-, *m*-, and *p*-dichlorobenzene at 120° and 180° in the presence of 0.276:1:1 mol. of aluminium chloride has been studied by some Russian workers; the equilibrium mixture contains *o*- 12%, *p*- 33%, and *m*-isomer 55% (11).

The kinetics of the sulphonation of isomers of xylene and ethylbenzene with sulphuric acid have been studied; the rate of sulphonation increases with increase in the r.p.m. of the stirrer up to a critical value, beyond which it remains constant. Apparently sulphonation occurs in the acid phase (12). In the disulphonation of benzene, sulphone formation can occur both from benzene and benzenemonosulphonic acid but not from the final *m*-disulphonic acid; sulphone formation is hindered by presence of sodium sulphate (13). In a study of the sulphonation of toluene, a method

is developed for determining toluene-*m*-sulphonic acid in a mixture of isomers, based on the conversion of the sulphonic acids into sulphonchlorides, nitration, saponification, reduction and bromination with a parallel determination of sulphuric acid and titration with a nitrite solution (14). *o*- and *p*-ethylbenzenesulphonic acids are prepared from ethylbenzene by direct sulphonation or from *o*-nitroethylbenzene; the m.p. diagram of the binary system of the nitro-*S*-benzylthiuronium salts of *o*- and *p*-ethylbenzenesulphonic acids was constructed to determine the composition of the mixtures (15). The kinetics and equilibrium of the mutual conversion between *o*- and *p*-toluenesulphonic acid were studied at various temperatures in aqueous sulphuric acid by the same author (16); the rate of conversion obeyed the first-order kinetic law. A novel process for the manufacture of resorcinol comprises alkali fusion of 2,4-dichlorobenzenesulphonic acid to the 2,4-dihydroxy-compound followed by desulphonation with dilute sulphuric acid (17).

When toluene is nitrated with mixed acid in presence of an oxidising agent like vanadium pentoxide or manganese dioxide, 2,4-dinitrobenzaldehyde is obtained in reasonably good yield (18). Phosphates of phenols when nitrated with mixed acid give nitrophenols with simultaneous saponification of the phosphate group (19); thus, tri-(*p*-chlorophenyl) phosphate dissolved in monohydrate and nitrated with a mixed acid (33 : 67  $\text{HNO}_3$  :  $\text{H}_2\text{SO}_4$ ) at 10° gave 4-chloro-2-nitrophenol. Preparations of a variety of *N*- and *p*-nitrosoanilines by mainly standard methods or slight variations of them have been reported (20). Ultra-violet spectra (in the range 210–280  $\text{m}\mu$ ) and infra-red spectra (in the range 1300–1600  $\text{cm}^{-1}$ ) have been investigated for all isomers of mono-, di- and tri-nitrobenzenes and nitrotoluenes (except 1,2,3-trinitrobenzene). Introduction of a second nitro group decreases the conjugation by increasing competition for electrons of the ring and results in a hypsochromic shift in the ultra-violet. The infra-red spectra show a splitting of the symmetrical band (of the nitro group) wherever one nitro group is strongly hindered. The asymmetric band frequencies fall into three ranges: mononitro 1509–1540  $\text{cm}^{-1}$ , dinitro 1539–1552  $\text{cm}^{-1}$ , and trinitro 1554–1567  $\text{cm}^{-1}$  (21).

A most interesting paper on the kinetics of the reduction of nitrocompounds by sodium disulphide has recently been published by Ogata and co-workers (22). The reduction of nitrobenzene by sodium disulphide to aniline has been studied kinetically between 30° and 60° in 70 and 10 vol.-% aqueous methanolic solutions with an ultra-violet spectrophotometer; the rate was found to be proportional to  $[\text{Na}_2\text{S}_2]^{1/2}$ . Production of the tolylenediamines has received considerable attention; of particular interest is catalytic hydrogenation in the molten state, using dinitro compounds containing less than 500 p.p.m. of nitrocresols, whereby the hydrogenation can be safely carried out at 90–135° at ordinary or slightly

elevated pressure, without the formation of tarry by-products (23). The catalyst employed is a palladium/charcoal or nickel/silica type and the dinitrotoluenes are used in the form of a slurry in de-ionised water. Aromatic amines are alkylated in the nucleus by reaction with an aliphatic olefin at elevated temperatures and pressures with a variety of catalyst mixtures like an aluminium compound of an aromatic amine and a metal halide (Al, Zn, Ti, B, etc.) (24).

The mechanism of amination of fluorochlorobenzenes by metal amides and aqueous ammonia has been studied by some Russian workers (25); reaction of *o*-fluorochlorobenzene with sodamide in liquid ammonia for 5 h. gave 83% *m*-fluoroaniline, whereas the use of 31% aq. ammonia in the presence of a little cuprous chloride for 6 h. at 250° gave 100% *o*-fluoroaniline.

Colour stabilisation of aromatic amines has formed the subject of a few patents. In one, unsubstituted phenylenediamines are stabilised by addition of 0.01-4% of elemental sulphur either before or after distillation (26a). In another, arylamines and naphthylamines are effectively stabilised against discoloration by the addition of a small amount of an acetoacetylarnide (26c), whilst in a third, the addition of 0.01-0.5% of ethylenethiourea, dibutyl tin oxide or dibutyl tin laurate has been suggested (26b). The acetylation technique for the determination of primary or secondary amines has been adapted to the direct photometric titration of aromatic amines which are unsubstituted or substituted with alkyl, alkoxy, hydroxy and halogen groups. The absorbance in the ultra-violet region of the spectrum is measured as a function of the volume of standard acetylating reagents (27).

The electronic structure of  $\beta$ -naphthylamine has been studied from the point of view of explaining its metabolic reactivity (carcinogenic activity) by French research workers. Static and dynamic structure indices were calculated by the LCAO method, and these were used to account for the chemical reactivity of the molecule. Certain aspects of its metabolic reactivity were explained by complex formation between  $\beta$ -naphthylamine and a cellular acceptor-element in the organism (28).

Benzonitrile is obtained by continuous vapour-phase oxidative ammonolysis of monoalkylbenzene in the presence of steam and catalysts like tin or titanium vanadate (29). High yields of aromatic nitriles are obtained by treating aromatic mono- and di-carboxylic acids, anhydrides, amides and imides with ammonia and a conventional dehydrating catalyst such as alumina, in such a manner as to minimise decarboxylation by limiting the time in a heated zone (30). A number of patents has been taken out on the reduction of aromatic nitro compounds with sodium and potassium amalgam. Thus, a continuous process for the preparation of *oo'*-hydrazotoluene is run in three stages: in the first stage, *o*-nitrotoluene is reduced to azotoluene, which is then treated in a second stage with



$\frac{1}{2}$  current strength and an alkali concentration of 40–59%, and finally in a third stage to give hydrazotoluene (31). Similar reductions of *p*-nitrotoluene and *o*-nitroanisole have also been described. Azo- and azoxy-benzenedisulphonic acids are prepared in very high yield by oxidising sulphanilic acid in alkaline solution with chlorine, hydrogen peroxide or oxygen in the presence of a catalyst like osmium tetroxide (32).

In a study of the kinetics and mechanism of diazotisation, Schmid & Woppmann (33) determined the velocity coefficient of the initial reaction during the diazotisation of aniline in perchloric acid and in buffered nitrite solution at 0°, 15° and 25° and used the data for the calculation of the free activation enthalpy  $G$ , the activation entropy  $S$ , and the activation enthalpy  $H$  for the temperature range 0–25°. The mechanism of the diazotisation of aniline has been studied spectrometrically in 66–74% sulphuric acid and 57–61% perchloric acid, under which conditions the stoichiometric nitrous acid is largely converted into ionised nitrosonium salts (34). The results appear to be inconsistent with any mechanism involving a rate-determining nitrosation of the amino group, and indicate that a new factor, the rate of proton transfer to the medium, can become important at high acidities. Thermal stabilities and infra-red spectra of some solid metal-salt-stabilised diazonium salts have been studied by measuring the rate of nitrogen evolution at 98° (35). A detailed review on the structure of diazo compounds has appeared in a Russian journal (36).

A continuous process for diazotisation of amines is described, whereby amines which diazotise relatively slowly because of their low solubility or coarse grain size can be re-circulated or made to react in a series of vessels arranged in a cascade (37). Nitrogen peroxide dissolved in a solvent like nitroethane is cooled to –70° and nitric oxide is passed in to give nitrous anhydride; gaseous boron trifluoride is then bubbled into the solution, giving the complex,  $\text{BF}_3\text{N}_2\text{O}_3$ , which reacts in organic solvents with even such weakly basic amines as 2,4-dinitroaniline to give the diazonium compounds in a dry, stable form (38). A mixture of a primary arylamine devoid of solubilising groups, an organic nitrite, a non-ionic and a cationic surface-active agent, and a water-miscible solvent has good stability and gives a clear diazo solution on acidification (39). It has been claimed that aromatic compounds other than primary amines react with nitrosyl derivatives of inorganic acids, in presence of an inert organic solvent to give diazonium compounds. Thus, 2-methoxy-5-nitrobenzene-diazonium sulphate has been prepared by the action of a solution of sodium nitrite in sulphuric acid on a solution of *p*-nitroanisole and mercuric oxide in sulphuric acid (40).

The reaction of diazonium salts with nucleophiles has been studied by various authors. In one study, rates of reaction of

various *o*- and *p*-substituted halogenobenzenediazonium ions with thiocyanate, which results in substitution of thiocyanate for halogen, have been measured by following the course of the reaction with  $^{14}\text{C}$ -labelled thiocyanate ion (41). In acidic aqueous solution tetrazotised *p*-phenylenediamine reacts with chloride, bromide, thiocyanate and azide ions to yield the corresponding *p*-substituted benzenediazonium ions at rates far greater than that of any reaction of the second diazonium group. The mechanism of these substitution reactions is believed to involve transition states with bonding  $\omega$ -nitrogen as well as carbon (42). The evidence on aryl-group migration in the nitrous acid deamination of amines was examined in so far as it bears on the problem of the mechanism by which nitrogen is lost; the relative rates of aryl migration and interconversion of rotational isomers of the open carbonium ion intermediates were calculated (43). The replacement of the diazonium group by the nitro group has been studied, and an improved preparation of *o*- and *p*-dinitrobenzenes described (44). The ionisation constants of the diazonium ion group in substituted benzoic and phenylacetic acids were measured potentiometrically and spectrophotometrically. The rates of bromination and coupling roughly support these data (45).

Oxidation processes, and the preparation of carboxylic acids, have again received considerable attention, many of the patents as usual relate to terephthalic, phthalic and isophthalic acids and are therefore considered in the chapter on 'Heavy Organic Chemicals' (see pp. 135-140 above). However, some of the processes can be of more general use, for example, the liquid-phase oxidation of alkyl-substituted aromatic compounds in organic acid medium in the presence of a metallic bromide and a ketone or other organic compound which forms a peroxide under the reaction conditions (46). In a process for making aromatic aldehydes from aromatic hydrocarbons and carbon monoxide, a complex metal fluoroborate is used as a catalyst (47).

### New intermediates

New bis-*p*-aminophenylbutadienes are prepared by condensing 2 mol. of *p*-nitro- (or *p*-acetamido-)benzaldehyde with 2 mol. of succinic anhydride and then reducing (or hydrolysing) the product (48). These compounds can be used as diamines in place of benzidine etc. for the preparation of disazo dyes. Dye intermediates for azo dyes substantive to cellulosic fibres are prepared by refluxing stilbene-4,4'-dicarbonyl chloride with J acid and pyridine (49). New coupling components (50) comprise substituted anthranilic acids,  $3,1,4\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{X}(\text{NH}\cdot\text{CHY}\cdot\text{CO}\cdot\text{NH}_2)$ , where X is H, Cl or Br and Y is alkyl or aryl. New aromatic amines suitable for diazotisation and conversion to azo dyes are prepared by condensation

of an isocyanate with a sulphonamide in a mixture of sodium carbonate and acetone or another non-hydroxylated solvent (51); examples are *N*-(3-amino-4-hydroxybenzenesulphonyl)- and *N*-(4-amino-3-hydroxy-6-methylbenzenesulphonyl)-*N'*-ethylurea. The preparation has been described of new intermediates comprising aromatic diamines with oxygen and sulphur bridges, such as 4-amino-4'-(*p*-aminophenoxy)diphenyl ether or thioether; they gave new yellow to brown to red cotton, nylon and rayon dyes (52).

### Naphthalene and acenaphthene intermediates

Naphthalenes are separated from hydrocarbon mixtures containing them by countercurrently contacting the mixture with an aqueous solution of a selective solvent for naphthalenes, such as a higher aliphatic alcohol, an alkylene glycol, polyalkylene glycol or an ether of such alcohol or glycol, at elevated temperature (53). Vapour-phase isomerisation of a 1-methylnaphthalene to naphthalene and dimethylnaphthalene over synthetic aluminosilicate has been studied (54); isomerisation proceeds rapidly at 270° and the rate increases with temperature up to 300-350°.

Naphthalene-2,6-disulphonic acid is obtained by heating a metal salt of the 2,7-disulphonic acid to at least 250° in an inert atmosphere and in presence of a catalyst like mercuric or chromium oxide (55). The migration of the alkylsulphonyl residue in alkyl 1-chloro-8-naphthyl sulphones has been investigated (56); apparently migration of  $\text{SO}_2\text{R}$  is a characteristic of only the 1,8-isomers and is associated with the space reaction of the peri-C distorting the valence angle at  $\text{C}_{(1)}$  and  $\text{C}_{(8)}$ .

Separation and identification of naphthol- and naphthylamine-sulphonic acids by descending paper chromatography and on alumina columns has been described (57, 58), and the  $R_f$  values of the main constituents and those of associated compounds are reported. A photometric method for determining naphthionic acid in technical 1-naphthol-1-sulphonic acid has been outlined (59). X-ray powder diffraction data are presented for 15 organic compounds (60); these permit the identification of the azoic coupling components of Naphthol AS, some of its derivatives and related compounds.

1-Hydroxy-2-*N*- $\alpha$ -(3-sulphobenzamido)ethylnaphthoamide is prepared by heating phenyl 1-hydroxy-2-naphthionate with excess of ethylenediamine, reacting the product with *m*-chlorocarbonylbenzenesulphonyl chloride and hydrolysing (61). New azo dyestuff intermediates are obtained by the action of 3-chlorocrotonic acid on aminonaphtholsulphonic acids like 1-amino-8-naphthol-3,6-disulphonic acid (62). New coupling intermediates for azo dyes have been described in which a radical of the biphenyl series is connected to the amino groups of two 6- or 7-amino-1-naphthol-3-sulphonic acids (63).

3-Bromo-, 3-chloro-, 4-chloro- and the unknown 4-bromo-acenaphthene were synthesised by thermal decomposition of the double salts of the 3- and 4-acenaphthenediazonium halides with a zinc halide (64). Nitration of acenaphthene with nitric acid of different concentrations and with mixed acid was studied in several solvents. The best results were obtained at 10–20° (65) when a yield of 99% was obtained with concentrated nitric acid. 4,5-Dichloro-2,7-dinitroacenaphthene was obtained in good yield by nitration of 4,5-dichloroacenaphthene (66).

### Anthraquinone and polycyclic intermediates

A review has been published on the photopolymerisation of the compounds of the *meso*-anthracene series (67). Syntheses of 3- and 1'-fluoro-1,2-benzanthracenes, 3-fluoro- and 4'-fluoro-10-methyl-1,2-benzanthracenes from 1-naphthylamine have been described (68). 6- and 7-fluoro and 6-methoxy-10-methyl-1,2-benzanthracenes have also been synthesised (69). It has been shown spectroscopically that the passage from 1,4-anthraquinone to the 2,3-dihydro-derivative results in the same change in the spectrum as is produced in the formation of the bisulphite adducts from 1-nitroso-1-anthrol and 1,4-anthraquinonedioxime. Thus, the latter substances react with sodium bisulphite in the quinoneoxime form and add the bisulphite across the double bond in the quinoidal form (70). An alkylated or arylated anthraquinol is produced by the catalytic hydrogenation of an alkylated or arylated anthraquinone in a solvent medium containing up to 10% of a chlorinated hydrocarbon (71). Sulphones of the anthraquinone series are produced by the action of aryl sulphinates on haloanthraquinones in Cellosolve (72).  $\alpha$ -Hydroxy- $\beta$ -nitroanthraquinones are produced by treating an anthraquinone, containing in the  $\alpha$ -position a halogen atom, a hydroxy group or a nitro group, and which is unsubstituted in the  $\beta$ -position, with a nitrite or a complex nitrite of an alkali metal and an acid in a water-miscible organic solvent (73). Good yields of bis-diazo compounds from 1,5- and 1,8-diaminoanthraquinones can be obtained by diazotising for 20 h. in conc. sulphuric acid at 0–5° with dry sodium nitrite (74). The addition of potassium bromide helps the diazotisation of all aminoanthraquinones. The  $R_f$  values of 24 aminoanthraquinone derivatives have been found (75) using four solvent systems on Whatman paper No. 3. The synthesis of 1- and 2-anthraldehydes have been investigated (76) by treatment of 1- and 2-anthronitriles with a deficiency of lithium aluminium hydride.

A new synthesis of phenanthrenes starting from cyclohexanone has been reported by Russian authors (77). Cyclohexanone is condensed with an acyl chloride and the resulting acyl-2-chloro-cyclohex-2-ene is then treated with ethylene glycol and KOH to give the monoethylene ketal of 2-acylcyclohexanone. This on

treatment with  $\text{CH}_3\text{Ph-MgCl}$  followed by cyclodehydrogenation, gives a 9-alkyl-1,2,3,4-tetrahydrophenanthrene, which is further dehydrogenated to a 9-alkylphenanthrene. The self-condensation product from 9-phenanthrenealdehyde regarded previously as 9,9'-phenanthroin was identified as 9,9-phenanthril (78). The true 9,9'-phenanthroin was prepared in good yield from phenanthrenealdehyde by treatment with potassium cyanide. The different types of deformation which may be affected in phenanthrene owing to the intramolecular steric impediments of some of its atoms were discussed in a recent paper (79). Both the deformation affecting only the sterically hindered atoms and that affecting the entire molecule were treated.

Alkali and alkaline earth metal derivatives of cyclopentadienes react easily with pyrylium salts to form 5-hydroxy- or 5-alkoxy-2,4-pentadienyldiene-fulvenes which split off water or alcohol with ease to give azulenes (80). Dicyanoethylation of 9-aminofluorene in acetic acid solution in presence of cuprous chloride has been described (81). Methylfluorenone derivatives were prepared by oxidation with selenium dioxide of the corresponding fluorenes, and their ultra-violet spectra are given (82).

### Heterocyclic intermediates

Investigations in the heterocyclic field have been many and varied, particularly because of the importance of heterocyclics in pharmaceuticals. A great deal of selection has therefore been necessary in preparing this review, and in general attention has been limited to work on fundamentally new structures, to reactions of general interest, and to new compounds specially described as dyestuff intermediates.

Derivatives of benzonaphthofuranol, particularly carboxyarylates, are coupling components for azoic dyes (83). The starting material is prepared by the condensation of 1 mol. of resorcinol with naphthaquinone in acetic acid containing a little sulphuric acid. A process is described according to which the reaction of a Schitt's base of the general formula,  $\text{RCH}_2\text{NR}'$  (where  $\text{R}'$  is a lower alkyl of 3 to 6 carbon atoms), with an aryl nitromethane in the presence of an aliphatic acid gives  $\alpha$ -nitroarylethylenes of high purity (84). Compounds like 2-(3-nitrostyryl)furan and 2-(2'-chloro-3-nitrostyryl)furan have been prepared by this method. The reaction of esters of acrylic, fumaric, and crotonic acid with sulphur, and the preparation of tetraphenylthiophens, was studied (85). The best method for the latter comprises interaction of benzil with dibenzyl ketone to give tetraphenylcyclopentadiene followed by heating with sulphur. Ultra-violet absorption spectra of 5-substituted-2-nitrothiophens and their vinyl analogues have been determined (86); the effect of the nitro-group was greater in the

corresponding furan series, thus demonstrating the more aromatic character of the thiophen ring.

Oxidation of 2-nitropyridine-5-carboxylic acid has been studied and the use of its esters in ester-type condensations investigated (87). The nitro-group proved to be very labile towards nucleophilic substitution. New 6-amino-8-hydroxyquinolines, e.g., 6-( $\beta$ -hydroxy-ethylamino)-8-hydroxy-2-phenylcinchonic acid, yield azine dye images by development with *p*-phenylenediamine followed by bleaching and fixing (88). The several steps in the synthesis of carbazoles by the Bischler reaction have been studied (89); the reaction of 2-chlorocyclohexanone with arylamines is best carried out in a high-boiling solvent (Cellosolve) in presence of sodium carbonate and a small amount of quinoline. The improved preparation of a number of substituted 1,2,3,4-tetrahydrocarbazoles was also reported.

Ultra-violet absorption spectra of haloindoles and haloindole-2-carboxylic acids have been tabulated and plotted for  $10^{-5}M$  solution. Introduction of halogen into the benzene ring does not modify substantially the indole absorption, whereas substitution in the pyrrole ring has effects varying with the position of the substituent (90). 2-Cyanoethylene-indolines are prepared by reacting a 2-methylindoline derivative with a cyanogen halide at elevated temperatures in presence of an inert solvent and an acid-binding agent (91). Indoline on nitration gives 6-nitroindoline in quantitative yield, and this on oxidation with chloroanil gives 6-nitroindole (92). Preparation of other halogeno- and nitro-indolines and indoles are also described.

5-Amino-3,4-dicyanopyrazoles are prepared by reacting a tetracyanoethylene with a monosubstituted hydrazine; the products are claimed to be useful in the syntheses of dyes and dyestuffs intermediates (93). A new and improved process for the well-known intermediate, 5-amino-3-methylpyrazole, has been described (94) in which  $NH_2NH\cdot CO_2Et$  is condensed with  $CN\cdot CH_2\cdot CMe\cdot NH$ . Reduction of 4-nitrosopyrazole by hydrazine hydrate gives either the 4-aminopyrazole or the 4,4'-azopyrazole according to the solvent used (95). In ethanol, the former is the main product, whereas in acetic acid the azopyrazole is obtained. Derivatives of 1-benzyl-5-pyrazolones substituted in the 3-position are described, the required benzylhydrazine being prepared from hydrazine hydrate and benzyl chloride (96). When phenylhydrazine is refluxed with acrylonitrile in butanol containing sodium, 3-amino-1-phenylpyrazoline is obtained in good yield (97). Various other derivatives of 3-amino-1-phenylpyrazoline are also described.

4-Nitro-*o*-phenylenediamine has been condensed with several aromatic aldehydes in acetic acid to give 2-aryl-1-arylmethylnitrobenziminazoles and 2-aryl-5-(or 6-nitro)benziminazoles (98). In many cases very good yields are obtained. Steric hindrance exists

in the quaternary salts of 2-(*p*-dimethylaminophenyl)benziminazole and its 1-methyl-analogue as shown by examination of their spectra in comparison with those of the sulphates of these bases (99). The same phenomenon existed in the quaternary salts of similar benzthiazoles, benzoxazoles and pyridines. Condensation of benzthiazolyhydrazines with acetoacetic ester leads to the formation of benzthiazolypyrazolones (100) which can be used for the synthesis of cyanine dyes. Synthesis of isothiazole (1,2-thiazole) has been reported (101) and numerous derivatives have been prepared. Two synthetic routes were used, one of which involves the oxidative cleavage of 5-aminobenzisothiazole.

The coupling activity of a number of diazotised heterocyclic amines with phenol ethers and with aromatic hydrocarbons has been investigated; derivatives of 1,2,4- and 1,3,4-thiadiazole possess a particularly high reactivity which surpasses that of diazotised 2,4-dinitroaniline (102). The synthesis of a number of bis-2-benzoxazoles, representing a new class in which the two benzoxazole nuclei are linked by simple alkylene or arylene chains, is reported (103). Polyphosphoric acid was used as condensing agent. 2-(2'-Hydroxyphenyl)benzoxazole is obtained by condensing *o*-aminophenol and phenyl salicylate (104); if the condensation is carried out in an inert atmosphere and the product is subjected to alkaline and acid purification, the luminescence of the product increases. The preparation of a number of asymmetric 2,5-diaryl-1,3,4-oxadiazoles has been described (105, 106). These compounds, obtained from intermediates of the type  $\text{ArCO:NH:N:CHAr'}$ , are claimed to be useful intermediates for the manufacture of dyes. Infra-red absorption spectra of a number of 1,2,4-oxadiazole derivatives have been reported (107). 1,3,4-Oxadiazoles, described as useful dyestuff intermediates, are prepared from a hydrazine compound and a carboxylic acid or ester in presence of phosphoric acid (108). *o*-Diamines of the benzene series, when treated with a dihalogenoacetic acid in acid medium and the resulting 2-(dihalo-methyl)benziminazole hydrolysed, give 2-formylbenziminazoles, also described as useful dyestuff intermediates (109). A new class of boron-containing heterocycles, borimidazolines, are prepared by condensing an alkyl- or aryl-boronic acid with *o*-aromatic diamines (110).

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## (2) Fluorescent brightening agents and ultra-violet absorbers

### Fluorescent brightening agents

The U.S. Tariff Commission gives the production in 1959 at 7 million lb. with sales at 6.9 million lb. valued at \$16.8 million, an increase by about 20% over the 1958 figures (1).

There has been increased activity in this field during the last 12 months. A number of interesting review papers describe the applications and uses of these compounds in various fields, viz., their use and application on wool textiles (2), on wash-and-wear cotton (3), the use of polyvinylpyrrolidone as a retardant, etc. (4). The evaluation of optical whitening agents fluorimetrically (5) and the degree of whiteness imparted by them to fabrics (6) have also been the subjects of many investigations.

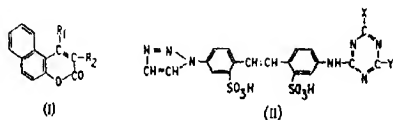
Among theoretical studies was that of the 'ortho effect' in 2-arylnaphthotriazole systems: a substituent in the *ortho* position causes a shift in the  $\lambda_{\text{max}}$  to shorter wavelengths and a reduction in the intensity of absorption, whilst electron-attracting groups in the *para* position cause an increase in both  $\lambda_{\text{max}}$  and in the intensity of absorption (7). The influence of various substituents in various positions of the anthracene nucleus on the displacement of the absorption and fluorescence spectra compared with those of anthracene has been studied by Cherkasov (8); with many poly-substituted anthracenes the value of the shift is equal to the sum of the shifts caused by each individual substituent. The quantitative relationship between the degree of deviation from coplanarity of the molecular configuration and the ultra-violet spectrum, as well as quantities such as the extra resonance energy and the band orders, have been determined for simple stilbene-type compounds by calculations based on the simple LCAO molecular orbital method (9).

A number of patent applications has been made based on variations of already well-known chemical types; thus, several patents (10) cover new substituents in triazinylstilbenes, one of the first classes to be used commercially as fluorescent brightening agents. They all claim special properties, such as stability to varying pH conditions, substantivity to different substrates, etc.

The coumarin structure has received more attention than of late. Benzcoumarin derivatives of the general formula (I) are prepared by reacting a hydroxynaphthaldehyde with a carboxylic acid or ester which contains a methylene group adjacent to the carboxyl group, e.g., malonic acid, cyanoacetic acid, acetoacetic acid, etc. (11a). Another variation (11b) covers coumarins and benzcoumarins having at position 3 a group,  $\text{CO}\cdot\text{Y}\cdot\text{R}_1\cdot\text{NR}_2\text{R}_3$ , where Y is O or NH,  $\text{R}_1$  is alkylene, and  $\text{R}_2$  and  $\text{R}_3$  are alkyl. When the group at

position 3 is phenyl substituted in the *para*-position by NH-COX (X is alkyl) the products are effective on polyacrylonitrile (11c).

Tetrazoles obtained by diazotising an aminostilbenetriazole and reacting with formylhydrazine have been claimed by Bayer (11d) as good whitening agents, as also have (11e) stilbyltriazoles of the type (II).



Quite a number of patents cover  $\alpha\beta$ -dibenzoxazolyethylene compounds, which, depending on their exact structure, are effective on a variety of synthetic fibres (12a). Fluorescent compounds containing a benziminazole nucleus have been extended to dibenziminazolythiophen derivatives (12b) and to dibenziminazolyfurans (12c), which are particularly suitable for whitening polyacrylonitrile. Brighteners for cotton and synthetic fibres of the dibenziminazoly pyrrole type have been patented by CIBA (12d).

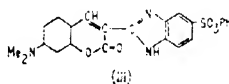
Azamonomethinecyanines have been claimed as bleach-stable brightening agents for cellulosic and synthetic fibres (13), and fluorescent anthradipyridazone compounds, which can be used as whitening agents for synthetic fibres either by incorporation at the melt stage or by treatment from an aqueous suspension, have also been reported (14).

### Ultra-violet absorbers

Interest in this field is rapidly increasing, as is evident from the number of new compounds reported and also from the improvement of methods of manufacture and slight structural alterations effected in already known ones. The structure and absorption spectra of a number of benzophenones have been studied (15). The ultra-violet and infra-red spectral changes on substitution are related to structural changes for a number of benzophenones on the assumption that benzophenone is initially non-planar, and that increased non-planarity may be caused by *o*-substituents. A process for preparing polyhydroxyarylphenones, according to which a hydroxyaryllecarboxylic acid is condensed with a phenol in the presence of a mixture of phosphorus oxychloride and zinc chloride, has been described (16). New products of the type 1,2,3,4-tetramethoxy-5-methyl-6-(3-methylbut-2-enyl)benzene, which are soluble in non-polar solvents and oils, absorb ultra-violet light and find use in sun-tan lotions (17).

Azole compounds in which the two carbon atoms adjoining the azole ring are also members of a benzene ring, and in which the

carbon atom situated between the two hetero atoms of the azole ring is linked to a carbon atom of a pyridine ring, have been described (18a). Azoles are also claimed (18b) in which two carbon atoms of the azole ring are simultaneously members of a benzene ring and in which the carbon atom between the two hetero atoms of the azole ring is bound to the carbon atom of another benzene ring which contains an etherified hydroxyl group in the *ortho* position to this link. New 2-phenylbenztriazole-1-oxide derivatives (19) are prepared by coupling a diazotised *o*-nitroaniline with a substituted phenol or aniline capable of coupling in the *ortho*-position and then treating with sodium dithionate to reduce and cyclise. New fluorescent compounds (20), which are useful ultra-violet absorbers, are coumarins having a heterocyclic substituent at position 3, such as (III).



Polycene compounds which protect photographic film compositions against ultra-violet light have been claimed by Agfa (21).

Finally, compounds of the type  $R-NH-C_6H_4-CO-CH_2\dot{Y}-X-p$ , where R is acyl, X is halogen and Y is a quaternary nitrogen, can be used in emulsions, waxes, oils, etc., for protection of the skin against ultra-violet light (22).

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## DYESTUFFS

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(Imperial Chemical Industries Ltd., Dyestuffs Division)

THE year 1959 saw a very considerable increase, over the previous year, in the value and quantity of the total exports of dyestuffs from the major manufacturing countries. This increase was accompanied by a decrease in the price per ton of dye, as shown by the figures in Table I (1).

Table I

Exports	1959			1958		
	Metric tons	Value, million dollars	Value, per ton, thousand dollars	Metric tons	Value, million dollars	Value, per ton, thousand dollars
Western Germany ..	27,093	87.5	3.16	21,270	68.0	3.19
United Kingdom ..	13,219	35.8	2.71	10,896	28.6	2.62
Switzerland*	11,000	36.1	3.28	8,582	29.3	3.58
U.S.A. ..	5,798	20.5	3.53	5,037	18.6	3.69
France ..	4,055	10.8	2.67	3,448	9.2	2.67
Japan ..	2,540	2.5	1.00	2,315	3.2	1.38
Total	64,314	193.2	3.00	51,548	166.9	3.24

\* Figures compiled from the imports of 18 countries given in (1).

The figures for the United Kingdom's trading in dyestuffs for the first eleven months of 1960 indicate that the trade expansion has continued. Thus for 1960 exports of dyes are estimated at 233.8 thousand cwt. valued at £11.7 million, compared with 211.6 thousand cwt. valued at £10.6 million for the corresponding period in 1959; during the same period imports have risen to 40.3 thousand cwt. valued at £4.0 million from 36.4 thousand cwt. valued at £3.6 million (2).

Academic work on dyestuffs during 1960 has covered a diverse range of topics and the flow of fundamental work, particularly from the Soviet Union, has been fully maintained. In the patent field, about 450 British, Belgian and U.S. patents have appeared, of which about 50% originated from Germany and 15% each from the United Kingdom, the United States and Switzerland. Particular emphasis has been placed on reactive dyes and these have now become well-established products; at least six reactive dye ranges are now commercially available (3).

The mechanism of dyeing has been considered from the point of view of molecular shape and the effect of steric influences on fastness properties, substantivity and uptake of reactive dyes discussed (4).

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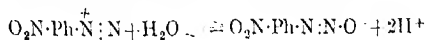
### AZO DYES

The year has seen the investigation of a variety of aspects of diazotisation and diazonium salts. In dilute perchloric acid the diazotisation of feebly basic aromatic amines is acid-catalysed and first-order with respect to both amine and nitrous acid (1). At high acidities, the rate-determining step in diazotisation appears not to be nitrosation of the amino group; a new factor, the rate of proton transfer to the medium, becomes important (2). The diazo exchange reaction, i.e., the establishment of an equilibrium



when a diazonium salt and an amine are mixed, had been thought to proceed via decomposition of the diazonium salt into amine and nitrous acid followed by rediazotisation. This mechanism is now untenable since exchange of nitrogen has been shown not to occur between isotopically labelled nitrous acid and a diazonium salt (3).

The structure of aromatic diazo compounds has been discussed (4) and the structures of some o-diazo oxides investigated; 4,6-dinitro-2-diazophenol and its 3-methyl- and 3-hydroxy- derivatives are quinonoid, whereas the 3-carboxy-derivative and 5-nitro-3-diazosalicylic acid are benzenoid in character (5). The hydration constant of the diazonium cation in the equilibrium



has been determined and calculated theoretically as  $7.95 \times 10^{-16}$  and  $6.3 \times 10^{-16}$  respectively (6). The diazonium salt-diazotate



equilibrium has been studied photometrically in relation to pH and a consistent scheme proposed for the changes involved (7).

The behaviour of the *p*-phenylenediaminebis-diazonium ion in water has been studied; at pH 2-4 it is in equilibrium with the mono-*anti*-diazohydroxide and mono-*anti*-diazotate; the mono-*syn*-diazotate is assumed to isomerise extremely rapidly and the mono-*syn*-diazohydroxide undergoes first-order decomposition to the phenol (8). In the *p*-phenylenediaminebis-diazonium ion there is a marked activation towards nucleophiles. Thus one diazonium group is replaced unusually rapidly by chloride, bromide, thiocyanate or azide ions (9). Similarly, the halogen atom in *o*- and *p*-halogenodiazonium salts is activated and susceptible to nucleophilic attack by the thiocyanate ion (10).

The photoisomerism equilibrium of azobenzene has been shown to be temperature-dependent (11), and whilst it has not proved possible to detect phototropism in aqueous solutions of *p*-amino- and *p*-hydroxy-azo compounds, it is readily detectable in solutions of *p*-alkoxyazo compounds; in these compounds the rate of reversion is slower in water than in alcohol or acetone (12).

Polysiloxane azo dyes have been prepared by using first or second components carrying trialkoxysilyl groups. The corresponding monomeric dyes, which may be prepared under substantially anhydrous conditions, polymerise in water. These polymeric dyestuffs have the hitherto unrecorded property of affinity for glass fibres and consequently can be used for dyeing this material (13).

#### *Water-soluble dyes for wool and nylon*

##### (1) *Reactive dyes*

Whilst not yet having achieved the same degree of importance as reactive dyes for cellulose, reactive dyes for wool and nylon have attracted considerable interest. Dyes of this class are, in the main, based on activated unsaturated compounds capable of undergoing addition reactions with the amino groups of the fibre. Typical activated unsaturated groups are the vinylsulphone (14), vinylsulphonamido (15a), and acrylamido (15b) groups. In addition, the methanesulphonyl esters of hydroxyalkyl sulphones and sulphonamides are reactive towards these fibres (16a). Halogeno compounds capable of undergoing condensation with the amino groups of the fibre are represented by the dihalogeno-*s*-triazinyl (16b), halogeno-acylamino derivatives of 1:2 metal complex dyes (16c) and chloroacetyl (17) dyes, and by the chloroacetamidomethyl compounds (18); these latter arise by condensation of a suitable dyestuff, e.g., orthonitric acid  $\rightarrow$  4-methylbenzoyl-H-acid with *N*-methylolchloroacetamide; in the example cited, condensation occurs at the 3-position in the pendant phenyl ring.

(2) *Non-reactive dyes*

(a) *Metal-free*.—In previous years, work on dyes devoid of anionic solubilising groups and solubilised solely by sulphonamide-type groups has been reported; dyes of this type give level dyeings from a neutral or weakly acid bath. Thus, *o*-arylsulphonylsulphamoylanilines diazotised and coupled on to naphthylamine-sulphonamides dissolve easily in hot water and can be dyed in this way (19). Recent patents have disclosed dyes which retain these good dyeing properties whilst being enhanced in solubility by the presence of one, or at the most two, sulphonic acid groups in conjunction with the sulphonamide-type group (20).

(b) *Metallised and metallisable dyes*.—Neutral-dyeing metal-complex dyes solubilised by sulphone, sulphamoyl and sulphonamide groups continue to attract interest (21); variations on these groups have been the ureidosulphonyl ( $-\text{SO}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ ) group (22) and the sulphamamido ( $-\text{NH}\cdot\text{SO}_2\cdot\text{NH}_2$ ) group (23). Much work has concentrated on mixed 1:2-chromium complexes for obtaining tertiary shades and blacks either devoid of anionic groups, e.g., the neutral dyeing black mixed 1:2-chromium complex from 4-nitro-2-aminophenol  $\rightarrow$  8-methanesulphonylamino-2-naphthol and 2-aminophenol-4-sulphonamide  $\rightarrow$  2-naphthol (24) or solubilised by a single sulphonic acid group (25, 26a). In the deep and tertiary shades obtainable from this latter type skitteriness is not noticeable and dyes such as the black mixed 1:2-chromium complex from 4-nitro-2-aminophenol  $\rightarrow$  2-naphthol and 4-(3'-sulphophenylazo)-3-methylaniline  $\rightarrow$  2-naphthol (26b) can be dyed in heavy shades from a neutral or weakly acid bath.

Some unusual first components have been used, e.g., *o*-hydroxyanilines carrying an oxazolin-2-yl or oxazin-2-yl group (27a) or an oxazolid-2-on-3-yl group (27b). The preparation of *oo'*-dihydroxyazo systems for metallisation by condensation of *o*-hydroxyphenylhydrazines with *o*-quinones, e.g., phenanthraquinone, has been described (28) and the dianils obtained by condensing arylazo-malondialdehydes with *o*-hydroxyanilines have been metallised (29). Treatment of an *o*-chloro-*o'*-hydroxyazo compound with copper sulphate, glycerol, sodium hydroxide and a sulphonamide yields the copper complex of an *o*-sulphonamido-*o'*-hydroxyazo compound; decoppering and re-chroming yields the corresponding chromium complex (30).

*Dyes for cellulose*

(1) *Reactive dyes*

Since the advent of the original chloro-*s*-triazinyl dyestuffs, reactive dyes for cellulose have rapidly increased in importance and now dominate the patent literature in this field. Intensive patenting of monohalogeno- (31) and dihalogeno- (32) *s*-triazinyl dyestuffs and also metallised halogeno-*s*-triazinyl dyes (33) con-

tinues; in this latter class, many patents refer to chromophores which are the copper complexes of appropriately substituted sulphonated arylamines diazotised and coupled with aminonaphtholsulphonic acids. Process details are given for the application of halogeno-s-triazinyl dyestuffs to the fibre in conjunction with resin-forming materials (34a). Replacement of a chlorine atom or atoms in these triazinyl dyes by negatively substituted aryloxy (e.g., *p*-sulphophenoxy) or arylthioxy groups (34b), by the thiocyno group (34c) or by the sulphonic acid group (34d) leads to products which are similarly reactive toward cellulose. The alternative halogeno heterocyclic systems based on pyrimidine have also attracted further attention, more examples of di- (35) and tri-halogenopyrimidinyl dyes (36) being disclosed.

Considerable interest has centred on halogenoacyl or halogenoacylamino dyes (37); compounds with groups such as  $\beta$ -chloroacetyl (38a),  $\beta\beta$ -dihalogeno or  $\alpha\beta\beta$ -trihalogenoacetyl (38b),  $\beta$ -halogenoacetyl (39),  $\beta$ -carboxy- $\alpha$  or  $\beta$ -halogenoacetyl (40) and 2-hydroxy-3-halogenopropyl or glycidyl (41) have been the subject of patent claims. In addition to vinylsulphones and their precursors such as  $\beta$ -sulphatoethylsulphones and chloroethylsulphones (42), other groups containing a sulphonyl linkage form the basis of reactive systems. Thus sulphon- $\beta$ -halogeno and  $\beta$ -sulphatoethylamido (43), sulphon-2-hydroxy-3-halogenopropylamides (44), sulphonfluorides (45) and sulphonethyleneimines (46) have supplied further classes of reactive dyes.

## (2) *Non-reactive dyes*

*Non-metallisable.*—It has been shown that the colour imparted by a multiplicity of azo linkages deepens as the number of such linkages increases to 3 or 4; subsequent increase in the number of links does not give further deepening and eventually leads to a decrease in intensity (47).

Tetrakisazo dyes have been prepared by linking aminodisazo dyes with terephthaloyl chloride (48) and disazos by linking aminoazos with phosgene or fumaroyl chloride (49).

*Metallised and metallisable dyes.*—The absorption spectra of benzidine disazo dyes having sulphonic acid groups adjacent to the azo linkages exhibit strained conformations due to repulsion between the sulphonic acid groups and the unshared electrons on the nitrogen atom. A similar degree of strain is exhibited by the coppered derivative devoid of adjacent sulphonic acid groups and hence the steric consequences of coppering are comparable with those of incorporating an *ortho* sulphonic acid group (50).

Blue-green, twice-coppered trisazo dyestuffs prepared by reducing a nitromonoazo dye (e.g., 1-chloro-6-nitro-2-naphthylamine-4,8-disulphonic acid  $\rightarrow$  2-naphthol-3,6-disulphonic acid) with glucose and sodium hydroxide are claimed (51a). Once-coppered

trisazo dyes formed by coupling two molecules of a diazotised amine on to the copper complex of 1,5,1',5'-tetrahydroxy-2,2'-azonaphthalene-7,7'-disulphonic acid are also reported (51b).

### Dispersed dyes

A new range of dispersed, polyester-soluble pigments has appeared in which the careful choice of substituents on conventional dye structures has led to high fastness properties and particularly good sublimation fastness (52).

2-Aminothiazoles continue to attract attention as diazo components. Those carrying 5-sulphone (53a) or 5-sulphonamide (53b) groups give, when diazotised and coupled on to tertiary amines, bright red shades of high fastness properties.

In addition to the sustained interest in hydroxyalkyl (54) and cyanoalkyl (55) groups as *N*-alkyl groups in conventional tertiary amine coupling components, the acyloxyalkyl group (56) is achieving some importance, particularly in combination with either an hydroxyalkyl or a cyanoalkyl group.

Reactive dispersed dyes based on the monohalogeno-*s*-triazinyl (57a) and dichloropyrimidinyl (57b) systems are claimed.

### Basic dyes

Basic dyes for polyacrylonitrile have been prominent, particularly when the quaternised nitrogen atom is incorporated in a heterocyclic ring system. 2-Aminobenzthiazoles have yielded benzthiazolium monoazo (58a) and disazo (on to arylamine, then on to phenolic or enolic coupling component) dyes (58b). Indazolium dyes are claimed by coupling on to 6-hydroxy- (59a) and 6-amino-indazole (59b) and quaternising, whilst imidazolium dyes result from 2-aminoimidazole diazotised, coupled and quaternised (60).

### Azoic dyes

*N*-Alkylated anthranilic acids carrying a nuclear sulphone (61a) or sulphonamide (61b) group are useful for stabilising diazonium salts as diazoamino compounds. The use of *N*-alkylated 4- or 5-sulpho-anthranilic acids enables soluble stabilised diazonium salts to be prepared from the more difficultly solubilised diazotised aminoazo compounds; these yield very deep shades on neutral steam development with 2,3-hydroxynaphthoic arylamides (61c).

Solid stable diazonium salts are obtained by diazotising 4-(nitrophenylazo)chloroanilines (62a) or 4-amino-2,5-dialkoxyazobenzenes (62b); the latter are useful for the azoic dyeing of Terylene in conjunction with 2,3-hydroxynaphthoic arylamides. The solid, stable diazonium salts from 2-amino-4,5-dialkoxy-2'-alkylsulphonylazobenzene are useful for obtaining green and black tints in azoic printing when applied with acetoacetaryl amides (62c).

## Pigments

Methods are described for the continuous production of azo pigments (63) and for their preparation under anhydrous conditions by kneading diazonium salts with coupling components together with small quantities of organic solvents (64). Filtration to give pigment press cakes of high solids content is said to be facilitated by heating pigment suspensions with methyl cellulose or methyl starch until flocculation occurs (65).

Heterocyclic first components such as 6-amino-2,4-dioxoquinoline (66a) and 6-amino-3,4-dihydrobenz-1,2,3-triazin-4-one (66b) have been used to yield insoluble azo pigments of high lightfastness, and diamines such as *N,N'*-di(aminophenyl)terephthalamides (67), 1,4'-diaminophenylureas (68) and *N,N'*-di-(3-aminophenylsulphonyl)phenylenediamines (69) have been used to secure very insoluble disazo pigments.

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*Pigments*

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**ANTHRAQUINONE DYES***Acid dyes*

Reactive dyes continue to provide the main patent disclosures in this field. The mono- and dichloro-s-triazinyl derivatives of 1-amino-4-(aminophenylamino)anthraquinone-2-sulphonic acid are most useful for obtaining bright reddish-blue shades (1); reactive dyes wherein the chlorotriazinyl residue is connected to the pendant phenyl ring through an aminoethylsulphamyl chain are also claimed (2). Introduction of a sulphonic acid group into the unsubstituted anthraquinone ring gives greener shades (3a).

Various other reactive groups have attracted attention: the  $\beta$ -halogenoalkylsulphamyl ( $\text{Cl-CH}_2\text{-CH}_2\text{-NH-SO}_2$ ) (3b) and acrylamido groups (4) are said to be reactive towards cellulose and wool respectively. Condensation of anthraquinone dyes with *N*-methylolchloroacetamide gives reactive  $\beta$ -chloroacetamidomethyl dyes for wool (5) and dyes carrying an isothiocyanate group on a pendant phenylamino can be heat fixed to cellulose (6).

1-Amino-4-bromoanthraquinone-2-sulphonic acid when condensed with an aminonaphtholsulphonic acid (e.g., H- or J-acid) gives blue dyes which possess excellent affinity for wool. Coupling with diazotised amines converts these blue dyes into useful violet dyes (7).

*Dispersed dyes*

The emphasis in this field remains on finding dyes of good affinity for synthetic fibres. This property is claimed in several patents dealing with 2-substituted derivatives of 1-amino-4-hydroxyanthraquinone. Thus the  $\omega$ -(dialkylamino)alkyl esters of 2-carboxylic acids (8), the 2-benzyloxy (9) and, e.g., the 2- $\beta$ -chloroethoxy (10) derivatives are said to have good affinity for synthetic fibres. 1-Amino-2-alkoxy-4-ethoxycarbonylaminoanthraquinones are also claimed to have good affinity, particularly for cellulose acetate (11).

**Reaction of 1-amino-4-hydroxyanthraquinone with acrylic acid,**



followed by esterification, yields 1- $\beta$ -alkoxycarbonylethylamino-4-hydroxyanthraquinone; the marked bathochromic shift is not accompanied by a drop in fastness properties as is usual in *N*-alkylation (12a). Condensation of 1,5 (or 8)-diamino-4,8 (or 5)-dihydroxyanthraquinones with *p*-bromophenyl alkyl sulphones (12b) or dialkylsulphonamides (12c) yields *p*-alkylsulphonyl- or *p*-dialkylsulphamyl-phenylamino derivatives which are blue dyes of good light fastness.

Basic disperse dyes are represented by trialkyl-1-alkylamino-anthraquinon-6 (or 7)-ylsulphonamidoalkylammonium salts (13a) and alkyl-(1-alkylantraquinonylamino)pyridinium or quinolinium salts (13b). The positive charge in these dyes leads to high affinity on synthetic fibres, particularly polyacrylonitrile.

In the reactive dye field, dispersed anthraquinones containing one or more  $\alpha$ -( $\gamma$ -bromo- $\beta$ -hydroxypropyl)amino groups are said to be superior in reactivity to the corresponding chloro compounds (14).

#### *Vat dyes and pigments*

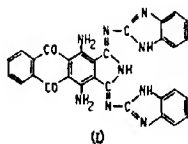
*N*-Methylation of phthaloylacridones has been shown to produce a hypsochromic displacement of the wavelength of maximum absorption and to reduce the affinity for cotton (15). The linear isomer of indanthrone has been synthesised by self-condensation of 2-amino-3-bromoanthraquinone or by condensation of 2,3-dibromoanthraquinone with 2,3-diaminoanthraquinone; it is a reddish brown, in contrast to the blue of indanthrone itself (16).

Several patents have appeared describing the linking together of amino-containing vat dyestuffs via a difunctional linking agent. Thus, *xx*-dichloro- $\beta\beta$ -diphenylethane-4,4'-dicarboxylic acid (17) and stilbene-4,4'-dicarboxylic acid (18) have been used for this purpose, the latter giving substantive products. 4-4'-Dichlorodiphenyl sulphone (19) and dihalogeno-3,4:8,9-dibenzpyrene-5,10-quinone (20) have been used to link two aminoanthraquinone or aminophthaloylacridone dyes and 2,4,7,8-tetrachloroquinazoline and 2,4-dichloro-6-phenyl-1,3,5-triazine have been used to link two dissimilar aminoanthraquinones (21). Yellow pigments arise when 1-aminoanthraquinones are linked by pyridinedicarboxylic acid chlorides (22) and aminoaccedianthrone linked by condensation with dichloroanthraquinones give fast brown shades on cotton (23a).

Dibenzaccedianthrone, obtained by cyclising the condensation products of 1,2-benzanthrone-9 and glyoxal are black-brown in shade as against the usual red-brown accedianthrone colour (23b).

Several methods by which heterocyclic rings can be built up on an anthraquinone molecule are described. Those from *o*-halogeno-nitroanthraquinones and 2-aminopyridine, pyridoimidazoloanthra-

quinones can be obtained. These are excellent orange pigments (24). Reaction of 2,3-dicyano-1,4-diaminoanthraquinone with amino-heterocyclic compounds gives isoindolenine dyes (e.g., I from 2-aminobenzimidazole) (25).



Cyclisation of the hydrazides of 1-aminoanthraquinone-2-carboxylic acids yields red 1-amino-2-(1,3,4-oxadiazol-2-yl)anthraquinone dyes for polyamide fibres (26a). Yellow indazole vat dyes arise from the condensation of 1,2-diaminoanthraquinones with benzaldehyde or dichloromethylbenzene (26b); the violet 3-phthalimido-4-methylbenzantrones and their derived carbazoles are useful for spin dyeing (27).

Reaction of 1-aminoanthraquinone with excess phthaloyl chloride gives not the usual dull red-yellow diamide but a bright greenish-yellow product which is not, apparently, either the phthalimide or phthalamic acid (28). The use of a mixture of aluminium chloride and an alkyl or *NN*-dialkylurea enables dibenzpyrenedione to be brominated at a lower temperature to give Vat Orange I in superior form (29).

Useful bluish-red to scarlet pigments are obtained by condensing perylene-3,4,9,10-tetracarboxylic acid with a variety of alkylated, arylated and halogenated anilines (30), and *N*-(chlorotriazinyl-aminosulphophenyl)imides of this acid or naphthalene-1,4,5,8-tetracarboxylic acid provide reactive dyes (31).

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## OTHER CLASSES OF DYESTUFFS

### *Phthalocyanines*

Continued effort on improving the process for making copper phthalocyanines in pigmentary form is shown by a number of patents relating to its manufacture and subsequent treatment (1). Stabilisation against flocculation is said to be achieved by salt milling in the presence of dialkylanilines (2a) or heteroaromatic bases (2b); incorporation of an insoluble metal salt of a sulphonated phthalocyanine and aluminium benzoate (3) or turbulent drowning of sulphuric acid solutions containing an aliphatic glycol (4).

Similarly, process improvements are described for chlorinated copper phthalocyanines (5).

Copper phthalocyanine containing hydroxyalkylaminomethyl groups on sulphonation gives dyes which have excellent wet fastness after heat treatment (6). Similarly, metal phthalocyanines oxidised with dichloramine T (7a) or, e.g., *N*-bromosuccinimide (7b) give fast dyeings on heat development. Reactive phthalocyanines are claimed, reacting by virtue of monochloro-*s*-triazinyl (8); di- or tri-chloropyrimidinyl (9); acrylamino or  $\beta$ -halogenopropionylanino (10);  $\beta$ -chloro- or sulphato-alkylsulphamoyl (11a) or  $\gamma$ -chloro- $\beta$ -hydroxypropylsulphamoyl groups (11b).

Phthalocyanine analogues have been synthesised in which one or two of the isoindole rings are replaced by *m*- or *p*-phenylene or 1,4-naphthylene residues. The products, which are soluble in hot organic solvents, show a marked hypsochromic effect; those with phenylene residues in place of isoindole exhibit a reversible colour change from yellow to red in the presence of acids, presumably due to the formation of onium salts (12a). Cleavage of the central N-Cu-N linkage in copper phthalocyanine, by forming a lithium complex, or shortening of this central linkage by replacing two peripheral nitrogen atoms by two double bonds, also shifts the maximum absorption peak to a shorter wavelength (12b).

#### *Indigoid dyestuffs*

Comparison of a series of 5-substituted 1-acenaphthenyl-2-thianaphthenylindigo dyes shows the absorption maximum to be shifted to longer wavelength by a 5-substituent in the order  $\text{Me} < \text{Cl} < \text{Br} < \text{I}$  (13). The deepest dyeing on cotton is obtained from the 5-methoxy derivative (14). 5- and 6-nitrothioindigo have been synthesised and the absorption spectra compared with those of thioindigo and dinitrothioindigo (15). Condensation of 9-chloro-3-oxo-2,3-dihydronaphtho(1,2-b)thiophen with 5,7-dibromoisatin gives a brown dye of good light fastness (16); a green-blue of good light fastness arises from condensation of 4-methyl-5-bromo-7-methoxyisatin- $\alpha$ -chloride with 5,7-dimethyl-3-hydroxy-1-thianaphthen (17).

#### *Triphenylmethane dyes*

The *ortho* positions in Michler's Hydrol Blue are not equivalent, those on the 'outside' being less sterically hindered. A progressive bathochromic shift and reduction in intensity is shown as methyl groups are progressively introduced in the 2, 2' and 2'' positions in Crystal Violet. The equivalence of the shifts indicates that the necessary rotational adjustments are shared between the aryl rings. The conformation of the 2,6-dimethyl derivative is discussed and evidence given against the existence of a conformational isomer of

Crystal Violet (18). Substituents introduced into the *o*-position on the unsubstituted phenyl in Malachite Green impart stability to the molecule (19).

The acid salts of basic triarylmethane dyes in which the salt-forming acid is an acid triarylmethane dye are said to be useful for the preparation of clean-to-handle carbon papers (20*a*). Condensation of Michler's hydrol with tris-(4-aminophenyl)methanes (20*b*), 10-(4-aminobenzyl)-3,7-bis-(4-dimethylamino)phenothiazine (20*c*) or alkylaminobenzoates (20*d*) give colourless compounds which become coloured in contact with acids, e.g., tannic or phosphotungstic acid, and consequently are of use for transfer sheets.

Amine-type tetrahydroxytriphenylmethanes derived from catechol when heated with amines *in vacuo* or oxidised in alkaline solution give deeply coloured fluorenequinones; these compounds can be reduced to colourless leuco compounds or metallised (21).

#### *Heterocyclic dyestuffs*

Cyanine dyes have attracted much attention from Indian and particularly Russian workers, fundamental work being done on the properties of cyanines of various structures, e.g., fluorine-containing cyanine dyes (22). Cell constants and space groups have been measured for 3,3'-dimethylthiacyanine bromide and iodide and 3,3'-diethylthiacarbocyanine bromide and iodide and the structure data correlated with other properties of cyanine dyes (23).

Useful pigments ranging in shade from yellow to black are obtained by condensing polyhalogenated isoindolones with diamines (24); polypyrazolone pigments of excellent resistance to solvents are obtained by condensation of bis-pyrazolones with chloroform, dialkoxymethyl esters, orthoformates or formamide (25*a*).

The acylation of leuco methylene blue with aromatic acid chlorides at pH 3-6 is said to give the acylated derivatives in superior form and excellent yield (25*b*).

The preparation of linear quinacridone pigments by condensation of dihalogenoterephthalic acids and arylamines has attracted further attention (26), as also has the cyclisation of the intermediate 2,5-di-arylamino-terephthalic acids (27). The bis-thiochromes corresponding to linear quinacridones are useful yellow pigments (28).

#### *Miscellaneous dyes*

Reactive nitro dyes, reacting by virtue of a chlorotriazinyl group (29*a*) or a  $\beta$ -halogenoethylsulphamyl substituent (29*b*) have been described. Insoluble styryl dyes for mass pigmentation are prepared by condensation of *p*-dialkylaminobenzaldehydes with cyanomethylsulphonyl derivatives of aromatic compounds (30). 1,1,3-

Tricyano-2-amino-3-aryliminopropanes have the property of imparting different colours on different fabrics (31).

A radiation-induced synthesis of Lauth's Violet by  $\gamma$ -ray irradiation of solutions of *p*-phenylenediamine and hydrogen sulphide is reported (32).

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## PHOTOGRAPHIC MATERIALS AND PROCESSES

### POLYMERS IN PHOTOGRAPHIC MATERIALS

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POLYMERS, which have always played a fundamental part in the production of light-sensitive materials, have found much wider application in the last two decades owing to the great progress made in both polymer and photographic science. However, a comprehensive review of the subject is lacking, although two short surveys by Kozlov have appeared in the U.S.S.R. (1). The emphasis of this report will be on recent progress in the design of polymers for film supports, colloids, and addenda in silver halide emulsions, and for light-sensitive non-silver systems. Limited space prevents a complete survey, and some applications, for example in electrophotography and in the diazotype process (1959 Report), will not be considered.

There has been some success in replacing well-tried polymers such as collodion (cellulose nitrate, used since 1850), especially in graphic arts materials, by purely synthetic compounds, but gelatin, first successfully used by Richard Leach Maddox in 1871, is still the preferred protective colloid for most silver halide emulsions.

#### Film base

The subject has been reviewed from the point of view of mechanical properties in a recent article by Calhoun (2).

#### *Cellulose derivatives*

The use of cellulose nitrate, similar to celluloid, as a film base was claimed by the Rev. Hannibal Goodwin in a U.S. patent application of 1887, but the patent (3) was granted only in 1898. Meanwhile, Reichenbach & Eastman patented a very similar support in 1889 (4). But cellulose nitrate film base is highly inflammable and has now been almost entirely replaced by cellulose acetate base. The theoretical maximum acetyl content for cellulose triacetate is 44.8%, and early materials had a content of 40%,



which has risen to about 43% in more recent products. Other esters have been considered, and in 1937 Eastman Kodak developed a base from cellulose acetate-propionate (30%–14%) (5).

The properties of cellulose acetate film are modified by the addition of plasticisers to increase flexibility. The dimensional stability of this film base is inadequate for certain applications.

#### *Polyesters*

Recent work has, therefore, been directed towards producing supports from the newer synthetic materials, especially those with low water absorption and temperature sensitivity. Poly(ethylene terephthalate), similar in structure to Terylene, has a high melting point, is very resistant to moisture and thermal deformation (6), and can be used without a plasticiser to make film base. It suffers, however, from the disadvantage that it is difficult to splice and scribe, and is subject to accumulation of static. Nevertheless, Du Pont have marketed 'Cronar', and Eastman Kodak have introduced 'Estar', both polyester supports.

Photographic films with high solidity and clearness and consisting of a mixed polyester of ethylene terephthalate (60–80%) and ethylene isophthalate (20–40%) are claimed by Goodyear (7). Caldwell (8) describes polyesters from a glycol, 4,4'-sulphonyldibenzoic acid and an  $\alpha$ -hydroxy-acid, while another Kodak patent (9) discloses polymers from 1,4-bishydroxymethylcyclohexane and terephthalic acid. Linear polyesters containing ether, thioether, carbonyl or methylene functions are described in a patent issued to Gevaert (10).

#### *Poly(esteramides)*

In several Kodak patents, polymers with ester and amide links are described. Thus, Caldwell (11a) claims polymers derived from *N*-hydroxyalkylamino-acids. A glycol and a simple diamine react with *N,N'*-bis-(*p*-carboxybenzoyl)alkylenediamine to form polymers which can be rendered water-permeable (11b). The products from the condensation of dibasic esters containing an amide linkage, for example bis-(*N*-ethoxycarbonylphenyl)adipamide, and glycols (11c), and linear polyester amides, which are useful for making orientable fibres and film base (11d), are other examples.

#### *Polycarbonates*

These have been used as supports for graphic arts materials and may find wider application in photography. Biphenols, treated with phosgene in the presence of bases, yield polycarbonate esters which in physical properties are equal to poly(ethylene terephthalate) film base (12), and in addition are readily soluble in such solvents as methylene chloride. Such a support was introduced by Agfa (13). Ansco produced a similar material under the name

'Plestar' (14). Modifications of the original Agfa patent, leading to even greater dimensional stability, are claimed for polycarbonates in which ether or thioether groups separate pairs of aromatic rings (15a). A number of further patents elaborate variations in the polycarbonate structure (15b).

#### *Styrene and acrylic derivatives*

Other types of polymers have been patented as film supports, such as polymers or copolymers of substituted styrene derivatives (16). Polystyrene itself must be stretched to reduce its intrinsic brittleness before it can be used as a support. A base, especially suitable for films used to reproduce maps with high accuracy, is essentially a poly(methyl methacrylate) (17). When 2-20% of an acrylic ester polymer is mixed with a methyl methacrylate- $\alpha$ -methylstyrene copolymer, extensibility and flexibility are much improved and a material suitable for film base is obtained (18a). Kodak (18b) have patented a continuous process for preparing photographic film where acrylonitrile and 0.5-15% of an acrylamide are used together with some preformed polymer of a similar type. Acrylonitrile is made to yield graft polymers suitable for base when polymerised in the presence of partially reacted polymers of *N*-(dialkylaminoalkyl)acrylamide or methacrylamide (19).

#### *Miscellaneous supports*

An interesting film support is described in another (20) patent. A polymer containing hydroxyl groups, for example, partially acetylated cellulose or polyvinyl alcohol, is reacted with monohaloalkyl isocyanate to form a monohaloalkylurethane derivative which can be quaternised with a tertiary amine.

Poly(vinyl chloride) and its copolymers have been claimed as supports, but suffer from the defect of temperature instability.

The search for new and better film base polymers continues to interest many manufacturers.

#### **Subbing compositions**

While the new polymer supports have excellent physical and mechanical properties, they present a very hydrophobic surface on which to coat the light-sensitive emulsion. Most photographic emulsions, apart from some graphic arts materials, are hydrophilic, and it is, therefore, necessary to coat the supports with a composition having powerful adhesion to both hydrophobic and hydrophilic surfaces. This is difficult to achieve with a single sub layer, and in consequence, many patents disclose the use of a series of sub layers with graded surface properties. It is convenient to classify subbing compositions according to the film supports for which they are designed.

*Polyester base subs*

In several subbing compositions for polyesters, polyvinyl derivatives form part of the main copolymer backbone. Vinylidene chloride and a small quantity of itaconic acid are copolymerised to provide subbing materials, in a series of Du Pont patents (21). After an oxidising treatment with alkaline permanganate, polyester base can be subbed with a vinylidene chloride-acrylic ester-acrylic acid copolymer (22). Agfa (23*a*) claim the use of mixed acetal polyvinyl polymers from benzaldehyde acetal, disulpho-benzaldehyde acetal and vinyl alcohol units. They also propose an unsaturated polyester composition derived from an aromatic compound with aliphatic hydroxyl substituents, and an aliphatic unsaturated dicarboxylic acid (23*b*). A low-molecular-weight amorphous polypropylene sub which contains other polymeric substances such as gelatin or nitrocellulose has also been described (24).

In a two-layer sub system from Du Pont (25), the lower layer consists of a thin coating of a polyester containing a polymethylene glycol (with 2-10 methylene groups) and poly(ethylene glycol) (with 1-5 ethyleneoxy groups), followed by a water-permeable colloid coating. Another two-layer sub for poly(ethylene terephthalate) supports (26) consists of a uniform dispersion of urea-formaldehyde resin, vinyl acetate-crotonic acid copolymer, and a pigment such as silica. This is overcoated with a hydrophilic polymer containing a pigment.

Perutz (27) have patented a three-layer sub system consisting of a thin layer of alkylmethyl methacrylate polymer, an intermediate layer of organic cellulose ester, and finally a hydrophilic colloid layer.

*Polycarbonate base subs*

Several Agfa patents on this topic have appeared. Three-layer subbing materials are described (28*a*) in which the support is coated with a vinyl chloride-vinyl acetate copolymer, or high molecular-weight mixed acetal polymers, perhaps with solubilising groups, or a mixture of a poly(vinyl chloride) copolymer with cellulose ester or cellulose nitrate. The middle sub-layer is cellulose nitrate or cellulose ester, and the top layer is gelatin, sometimes containing phthalic or salicylic acid, and glyoxal.

In another process (28*a*), a mixture of polycarbonate and nitrocellulose or ethylene vinyl acetate copolymer is claimed. An additional coating of a poly(vinyl acetal) with free hydroxyl group is optional.

Hydroxylic polymers, for example, vinyl chloride-vinyl alcohol copolymers with components or additional copolymers derived from vinyl compounds of which one constituent may be saponifiable, are the subject of another Agfa patent (28*b*).

*Polystyrene base subs*

Methacrylates key on to polystyrene and, mixed with more hydrophilic polymers, appear in several subbing compositions. According to Ilford patents, oriented polystyrene support can be subbed with poly(methyl methacrylate) or methacrylic acid-alkyl methacrylate copolymer (29*a*), and oriented polystyrene-acrylonitrile film base with methyl methacrylate-methacrylic acid copolymer (29*b*). These subs require additional layers of cellulose nitrate, followed by gelatin, before the light-sensitive emulsion is coated.

Subs for polystyrene base (30, 31) consist of a polyester from a glycol and an  $\alpha$ -unsaturated dicarboxylic acid, and also a terpolymer of butyl methacrylate, methyl methacrylate and methacrylic acid with 5-10% of a chromium salt.

*Polyvinyl base subs*

According to a Japanese patent (32), film supports of poly(vinyl chloride) or derived copolymers may be subbed with a mixture of vinylidene chloride-vinyl acetate copolymer and cellulose acetate, applied as a solution in acetone, benzene and tetrahydrofuran. Agfa (33) disclose a similar composition for poly(vinyl chloride) film base consisting of vinyl chloride-vinyl acetate copolymer and nitrocellulose or a cellulose ester, but a further thin layer of the cellulose derivative is added.

For certain emulsions containing poly(vinyl alcohol), Gevaert (34) claim a subbing layer composed of polymers such as polystyrenesulphonic acid or styrene-maleic acid copolymer, with the possible addition of gelatin.

**Gelatin replacements and extenders**

Gelatin replacement has received considerable attention. Gelatin, a natural product which varies considerably with source and refining, has a number of fortunate photographic properties, and so far there is no single synthetic material to equal its combined action as a protective colloid, halogen acceptor, sensitiser, and retarder.

*Peptising agents*

Gelatin acts at the silver halide precipitation stage as a peptising agent, and after precipitation, as a binder or film-forming substance. Replacements rarely fulfil both functions satisfactorily, except in slow materials. Poly(vinyl alcohol) is an adequate peptising agent, but restricts grain growth, so that its use is limited. Poly(vinyl alcohol) has been used as a peptiser and binder in a particle-tracking emulsion (35), and in a multilayer colour print material (36). Sodium cellulose sulphate is a peptising agent

which permits subsequent Ostwald ripening of silver halide grains in the dispersion (37); the binding medium is poly(vinyl alcohol). Ilford patents (38) describe ammoniacal emulsions in which the silver halide is initially dispersed in poly(ethylene glycol) derivatives, and is subsequently washed and redispersed in gelatin.

Materials containing copolymers of acrylic acid or its derivatives are useful both as peptisers and film-forming vehicles. Thus, a copolymer of acrylamide- $\beta$ -methacrylamidoamino-acid betaine with a poly(vinyl alcohol) acetal (39), a copolymer of acrylic acid-acrylonitrile with some other monomer units (40), mixed copolymers of butyl acrylate-styrene (or acrylonitrile) and methacrylamide-acrylic acid (41), and 2-vinylpyridine-methacrylic acid copolymer (42), are examples of complete gelatin replacements.

Polymers with structures more closely related to the gelatin they are intended to replace, are described by Eastman Kodak (43) and Ilford (44). These are, respectively, linear polyamides with extralinear hydroxyl groups, and synthetic polypeptides derived from *N*-carboxy- $\alpha$ -amino-acid anhydrides. In an effort to improve the properties of low-grade gelatin, gelatin graft polymers with hydrophilic and hydrophobic monomers have been synthesised (45). The peptised dispersion of silver halide in such a medium can be coagulated at pH 3.5-5, and the coagulum is redispersible in water.

#### *Silver halide dispersion vehicles*

Many polymer vehicles, compatible with gelatin, are available to extend the concentrated digested gelatino-silver halide emulsion, and to act as film forming substances. The property of reversible gelation is desirable, but not always essential, for the vehicle. Some polymers designed to replace gelatin do not gel in solution and in consequence require stronger conditions of drying at the film forming stage.

In addition to the film-forming polyvinyl derivatives mentioned in the previous section, poly(vinyl butyral) has been used as a binder (46a), and 1% starch amylopectin has been used to replace gelatin (46b).

In a Kodak patent (47), a binder which allows subsequent hardening of the layer to occur, consists of a poly(vinyl alcohol) derivative substituted with cyanoacetyl groups.

It is also possible to disperse the aqueous peptised silver halide in a water-permeable polymer in an organic solvent. This modifies the drying or setting properties of the cast film. Ethyl cellulose has been claimed as such a polymer vehicle (48), and Gevaert (49) describe a process in which an aqueous silver halide emulsion is dispersed in a hydrophilic binder, this in turn being dispersed in a non-aqueous solution of the vehicle, a vinyl chloride-vinyl acetate-maleic anhydride copolymer. Such an emulsion can be dispersed in a mixture of water and organic solvents (50).

Several patents disclose polymers for partial gelatin replacement. The addition of a Du Pont butadiene-acrylonitrile copolymer (51) reduces blistering and deterioration of film illuminated in high-intensity arc-lamp projectors. An Agfa copolymer of acrylonitrile with an olefinic monomer (52) improves colour emulsions containing anionic dyes. The emulsion polymerisation of amide, ester and styrene monomers gives a hydrosol compatible with gelatin (53). A partial replacement (54) consists of an olefinic monomer with urea, a methylol compound and a cellulose derivative, or a gelatin graft polymer.

### **Polymeric emulsion addenda**

Polymers have a variety of uses as addenda in black-and-white and colour emulsions.

#### *Sensitisers*

General Aniline (55) and Du Pont (56) claim considerable speed increases if a poly-(*N*-vinyl-lactam) is added to an emulsion; polyvinylpyrrolidone is specifically mentioned. Poly(ethylene glycol) and its derivatives are also claimed as non-optical sensitisers or development accelerators (57). Some of these compounds tend to cause increased fog on storage but this can be checked by the addition of antifoggants (58). In a poly(ethylene glycol)-sensitised emulsion, polyvinylpyrrolidone behaves as an antifoggant (59). A 'tin-protein' acts as a sensitiser, according to Gevaert (60a).

#### *Hardeners*

Some novel polymeric hardeners have been described. Gevaert (60b) found that oxidised polysaccharides containing aldehyde groups are excellent hardeners. A dialdehyde starch, 'Sumstar', recently marketed by the Miles Chemical Co. (61), is said to have a readily controlled hardening action. Another Gevaert patent (62) describes the half esters of malic acid with poly(vinyl alcohol) or cellulose as non-wandering hardeners for multilayer materials.

#### *Colour couplers*

Polymeric colour formers have been known for some time. Du Pont (36) have patented a range of poly(vinyl acetals), for example those derived from phenolic aldehydes (63), which react with oxidised colour developer to form polymeric dyes. Polymeric couplers have been devised from couplers containing amine groups and a polymer with recurrent acid anhydride groups (64).

#### *Mordants*

Dyes are frequently required in specific layers of light-sensitive products, for example in filter, masking and antihalation layers. Polymeric mordants are, therefore, finding wider application in

these materials. Since most of the dyes are anionic, the mordants are basic, usually containing amino-groups. Basic mordants prepared by Kodak (65) are condensation products of a poly(vinyl alkyl ketone) and an aminoguanidine. Gevaert patents disclose polymers with free amino groups, from a hydrolysed poly(vinyl carbamate) (66*a*), and products from the reaction of polynitriles with hydroxylamine (66*b*). A poly(methacrylic ester), substituted with quaternary ammonium groups, is a Du Pont mordant (67*a*). A similar polymer together with metal ions is used in a Du Pont dye transfer process (67*b*). A light-polarising film developed by International Polaroid (68) contains a polymer bearing free amino-groups, derived at least partly from polyvinylamine.

#### *Miscellaneous addenda*

Hydroxyethyl cellulose, partially esterified with a dicarboxylic acid, is claimed by Kodak (69) as a plasticiser which prevents desensitisation due to kinking and the loss of density which occurs when a processed layer dries down.

Stain is produced in colour film by the reaction of oxidised developer with incorporated couplers. This can be reduced by adding the condensation product of a polycarboxylic acid and gentisamide or homogentisamide (70).

An interesting method of intensifying a silver image is claimed by Oster (71). Semiquinones, or free radicals, which are intermediate oxidation products of aromatic amine developers, can catalyse polymerisation. Therefore, a vinyl monomer is introduced into the developer, polymerises on development, and the polymer so formed prevents aggregation of developed silver, thus increasing the optical density.

#### **Additional polymer layers**

Films and plates may be backed with an antihalation layer. The medium for the antihalation dyes is a polymeric composition which is preferably soluble in developer solutions. Polymers such as polyacrylic acid, styrene maleic anhydride, and poly(vinyl phthalate) have been used for the purpose (72).

A Russian paper (73) describes the use of cellulose acetate phthalate, and patents from Agfa and Kodak claim alkali-soluble backing vehicles consisting of copolymers of acrylonitrile, vinyl butyl ether and a maleate or fumarate ester (74*a*), polycarbonates (74*b*), and an interpolymer of vinyl acetate and maleic anhydride treated with glycollic acid (75) and an alcohol.

#### *Antistatic layers*

Electrostatic charges accumulate on the surface of film during manufacture and handling, and, if they are not dispersed, their discharge causes fogging and deterioration of the product. In a

number of patents it is claimed that an additional layer of certain polymeric materials, all of which are poly-salts, greatly reduces these harmful effects. Alkali metal sulphonate derivatives of a poly(vinyl acetal) (76) and of polystyrene or polymethylstyrene (77) have been used for this purpose. The latter polymers contain some sulphonamide groups, and require the addition of polyvinylpyrrolidone or partly saponified poly(methyl acrylate) to improve adhesion to a cellulose acetate support. General Aniline (78) propose a backing layer consisting of alkali metal salts of a fatty acid and a styrene-vinyl ester-acrylic acid copolymer. Sodium carboxymethylcellulose is suggested by Schleussner (79). Kodak (80) claim cationic polymers containing pyridinium or quaternary ammonium salt groups as excellent antistatic layers.

#### *Supercoats*

Some films are supercoated with a gelatin or synthetic polymer layer for protection against abrasion or ultra-violet light, or to obtain a special effect. For example to impart gloss, a supercoat of polyvinylcaprolactam or polyvinylpyrrolidone has been suggested (81). Post-development stabilisation of a photographic emulsion can be effected by treatment with a solution containing conventional stabilisers and a film-forming polymer (82). Gevaert (83) have patented alkali-soluble nitrated styrene maleic anhydride copolymers as binders for anti-abrasion, antihalation, antifogging and ultra-violet light-absorbing layers.

The formation of Newton's rings can be prevented by adding a supercoat of gelatin containing an alkali-soluble methacrylic acid-methyl methacrylate copolymer, according to Kodak (84). Two Kodak patents disclose polymers useful in ultra-violet absorbing layers. In one (85), hydrazones or thiazolidones which absorb strongly in the 260-400m $\mu$  range, are joined indirectly to the polymer backbone by ester or amide links. In the other (86a), thiazolidone rings are joined through acetal groups to poly(vinyl alcohol).

#### **Polymers in non-silver light-sensitive systems**

This section deals with some non-silver systems, not included in last year's report. Polymers act in light-sensitive non-silver processes, both as binders and as light-sensitive elements. Bitumen was used as the photosensitive element in the original Niépce process, and is still occasionally used in graphic arts materials. In many synthetic polymer systems a sensitiser, which generates free radicals, is used to increase the photosensitivity of the product.

#### *Cinnamate systems*

A specification from Eastman Kodak described a system based on cinnamoylated polystyrene (86b). Cinnamate esters of poly(vinyl



alcohol) (87*a*) and cellulose are alternative media, and many additional sensitisers (87*b*) are reported. The properties of these compositions (88) and of some derived commercial products (89) have been reviewed. Cinnamate polymers can be rendered soluble in alkali by reaction with dicarboxylic acid anhydrides (90*a*). Light-sensitive polyesters, derived from glycols and dicarboxylic acids such as cinnamylidenemalononic acid, can be sensitised with ketones and thioketones to yield high-speed resists (90*b*).

Farbenfabriken Bayer have patented a number of cinnamate compositions. Reactive isocyanate groups in  $\beta$ -arylacrylic acid derivatives condense with poly(vinyl alcohol) and other polymers to form light-sensitive materials (91). Alternatively, the polymer is built from a polyisocyanate, such as glycol di-(*p*-isocyanatocinnamate), and glycol.

#### *Chalcone systems*

The preparation of light-sensitive polymers from an aromatic aldehyde and polyvinylacetophenone has been published by Unruh (92). Further chalcone materials are prepared by condensing a hydroxychalcone with styrene-maleic anhydride (93*a*), or other maleic anhydride copolymers (93*b*). Polymers from poly(vinyl alcohol) or a polycarboxylic acid and a cinnamic acid or chalcone appear in a Bayer patent (94*a*). Light-sensitive lacquers containing copolymers derived from monomers with isocyanate groups and hydroxychalcones (94*b*) are another Bayer invention.

#### *Stilbazole systems*

Another system is based on the photosensitivity of stilbazolium compounds. Polymers derived from *C*-vinylpicolinium salts condense with aromatic or heterocyclic aldehydes, and the products may be sensitive to visible light (95*a*). Poly(vinyl alcohol), partly esterified with a sulphonic acid, reacts with  $\gamma$ -picoline, forming a polymeric quaternary salt; the latter can be condensed with aldehydes to yield stilbazolium polymers (95*b*).

A photographic printing process with light-sensitive polymers such as a styrene-maleic anhydride ester of 4-methoxycarbonyl-4'-(2-hydroxyethoxy)chalcone or a polyvinylstilbazolium salt, as mordants, is described by Tupis (96*a*). A paper coating of the polymer is exposed, bathed in ammonia, rinsed in water and then treated with an aqueous dye solution.

#### *Azide systems*

Interest continues in many light-sensitive azide processes. Eastman Kodak (96*b*) claim aromatic bis-azides to insolubilise styrene-butadiene copolymers. Water-soluble polymers, for example acrylonitrile-acrylic acid copolymer, can be rendered light-sensitive with 4,4'-diazidostilbene-2,2'-disulphonic acid (97*a*).

Azide substituted polymers and additional sensitisers (97b) are claimed for such lithographic systems. A coloured image-transfer system consisting of an azide-sensitised supercoat on a coloured gelatin layer is patented by Kodak (98). A Bayer patent (99) deals with compounds such as azides which are rendered capable of reaction with other molecules, for example di-isocyanates, by the action of light. Neugebauer & Reichel (100a), on behalf of Kalle & Co., who pioneered the use of azides, describe a light-sensitive layer consisting of a polyamide and an alkali-soluble azide. Acrylic polymers can be sensitised with sulphoniminoquinone-1,1-diazides (100b).

#### *Systems with separate cross-linking molecules*

Du Pont have devised a process in which soluble polymers react, on exposure to light, with small cross-linking molecules to give insoluble products. An initiator such as diacetyl, benzoin or benzil is added.

A wide range of polymers, including cellulose derivatives (101a), alkali-soluble polyvinyl derivatives containing oxy-acid groups (101b), polyamides (101c), neutral polyvinyl ethers, esters or acetals (101d), polyesters (101e) and polyurethanes (101f) are suitable. A composition of one of these polymers with a cross-linking agent such as glycol diacrylate or methylenebisacrylamide and an initiator, can be exposed and developed to provide a printing relief. Time Inc. (102) disclose a similar material based on polyamides.

In a variation of the process (103a), a polymer with amino-groups, for example  $\beta$ -diethylaminoethyl methacrylate polymer, is cross-linked by a complementary salt-forming monomer, methacrylic acid. The difference in solubility between exposed and unexposed polymer is enhanced in a process involving polyvalent metal chelate cross-links between the polymer chains (103b). The solvent developer is acetylacetone or hydrochloric acid in an organic solvent mixture.

#### *Dichromate system*

The well-known dichromate process relies on the action of chromium salts to render gelatin or cellulose derivatives insoluble on exposure to light.

Recent patents describe the use of dextrans (104), alkyl vinyl ether-maleic anhydride copolymer (105), partly oxidised starch or dextrin derivatives (106) and alginates (107) as media. Chromium complexing agents prolong the life of the unexposed plates (104c).

#### *Systems utilising monomers*

A process (108a) has been developed for the photopolymerisation of monomers in the presence of water with a catalyst mixture of

silver halide, a water-soluble silver salt and an amphoteric oxide. This is the basis of a reflex copying system (108*b*). In a closely related composition (108*c*) a colloidal binder contains a vinyl monomer and a catalyst mixture of zinc or titanium oxide with a mercury, thallium or iron salt; other organic catalysts are active.

#### *Miscellaneous systems*

The first group depend upon the action of light to initiate a chemical insolubilisation reaction. A Du Pont system consists of a poly(vinyl acetal) or ester with ethylenically unsaturated substituents, and a sensitiser (109).

Time Inc. (110) describe a photosensitive powder for use in the manufacture of moulded or extruded objects. It contains an ethylenically unsaturated polyamide, an inhibitor and an initiator of the benzoin type.

Schröter (111) obtains photosensitive coatings from poly(vinyl alcohol) or cellulose condensed with anthracene-9-aldehyde or a light-sensitive heterocyclic compound. The photodimerisation of anthracene is well known. Nitrothiophens render polymers insoluble on exposure to light according to Kalle (112).

Ferric compounds can be used to activate the insolubilisation process. In a recent specification (113) a coating consists of poly(vinyl alcohol) or methyl vinyl ether-maleic anhydride copolymer together with citric acid and ferric ammonium salt. The developer is dilute hydrogen peroxide solution.

Oster has succeeded in cross-linking a substantially saturated polyethylene polymer by very-short-wave ultra-violet irradiation. Unreacted polymer is removed with hot solvent (114).

Two systems depend upon light-sensitised polymer breakdown. Photodegradation of poly(methyl methacrylate) in the exposed areas by contact with a supercoat of a free-radical initiator is the basis of an intaglio printing method (115).

An interesting image transfer system recently described (116) comprises a hydrophobic aluminium sheet coated with lubricating oil, placed in contact with a carrier sheet containing a diazonium tetrafluoroborate salt. The latter releases hydrogen fluoride in the exposed areas, to produce a hydrophilic image.

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## EXPLOSIVES

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### Introduction

THIS report covers publications dealing with explosives in the last two years. Once again, the amount of literature remains at a high level; a large number of reports of work done under contract to, or in the laboratories of, the United States Government is being released, covering a period of more than ten years' work.

The amount of work on rocket propellants has not diminished, while, in the field of civil mining and blasting, the use of ammonium nitrate-fuel oil mixtures has become a paramount field of development activity.

### Nitroglycerine and other nitric esters

The manufacture of nitroglycerine has been described by Stettbacher (1), including developments of the Biazzi method. Redox potential measurements used in glycerine nitration are treated in some detail by Oehman *et al.* (2), but the interpretation of the measurements involves complex discussion.

A process developed by Nitroglycerin A.-B. uses injector nitration, followed by centrifuging to separate the product; it has been operated at Gyttrorp, and cuts down the amount of nitro-body in the actual nitrator to a nominal amount (3).

The present trend is toward the increasing use of synthetic glycerol (4) and Olin Mathieson will shortly synthesise their whole requirement (5). A process using tube nitration, oleum and recycled acid is covered by a patent of Imperial Chemical Industries Ltd. (6).

The use of polythene tubing for the transfer of nitric esters has been described by the same firm (7); handling by eductor has also been recommended on safety grounds (8).

For the polarographic determination of nitroglycerine (9), the use of a cathode ray polarograph is desirable. On admixture with aromatic compounds and sulphuric acid, nitroglycerine is capable of causing nitration (10).

Ethylene glycol dinitrate has been subjected to considerable toxicological investigation (11); one worker concludes that skin absorption is more important than inhalation.

The preparation of various diols, triols, and others up to hexitols is outlined by Machell (12) and dinitrates of tetra-, penta-, and

hexaethylene glycols have been made (13). Safer explosives are obtained by nitration of polyol ethers in mixture with glycerol and glycol (14), by addition of crystalline components to liquid nitric esters (15), or by nitration of polyethylene glycol (16).

*O*-nitration of methanol, glycol and glycerol has been studied kinetically and interpreted (17) in terms of nitronium ion attack. Other *O*-nitration studies in acetic anhydride, aqueous perchloric acid and aqueous sulphuric acid have been carried out by Bonner and his co-workers (18).

The nitrates of the lower alcohols are of interest as rocket propellants and the heat of formation of methyl nitrate (19) has been determined. Normal propyl nitrate can be used as a mono-propellant, and storage tests and other stability tests have been reported (20). Isopropyl nitrate is the subject of other patents (21).

Among the compounds obtained by nitration of natural products, nitro-starch has been prepared by Amoretty (22) and a prescription for its safe processing has been given (23). It may be stabilised by addition of alcohols containing more than three carbons (24, 25).

Pentaerythritol tetranitrate (PETN) is pre-eminent among solid nitric esters for explosive use: wartime studies of its stability have just been published (26). The production of the requisite tetrol is more difficult to achieve in good yield than is its subsequent esterification. The use of an ion-exchange catalyst for the condensation of formaldehyde and acetaldehyde enables continuous production to be carried out (27); the catalysts used include various peroxides and azo-bodies (28). Methods of eliminating formoses and resins from the reaction have been described (29).

Coating methods for making PETN conducting and improving the flow properties have been patented (30).

A number of explosives, including PETN, TNT and nitro-cellulose may be obtained in desired forms by solution in acetone and precipitation in water (31*a*). The protection of PETN against heat up to temperatures of 800° is effected by coating it with concrete (31*b*); when incorporated in sheets with nitrocellulose, PETN gives a product of a sensitivity low to shock, but high to primer (32).

Pentaerythritol trinitrate has been used in nitrocellulose propellants, in which it may be determined polarographically (33).

Triptaerythritol octanitrate is not easily obtained pure, but may be of use, in admixture, as a plasticiser for cellulose nitrate (34).

### Propellant explosives

The interest in rocket propulsion has once more been reflected by a large volume of published information on the subject; a con-



siderable amount of United States Government research work has been released for publication, some of which represents recent work and some concerns older work now made public. The total volume of information on orthodox propellants still remains high.

#### *Nitrocellulose*

The continuous nitration of cellulose is described in a number of publications by Hercules (35), and Wasag (36*a*) who use directed flow of the reaction mixture, which is subjected to stirring by ultrasonic means. A further patent describes the recovery of waste acid from nitrocellulose by a centrifugal process (36*b*). The use of magnesium nitrate in nitrocellulose nitration is elaborated by Hercules (37). Belgian work also describes advances in the continuous nitration of cellulose (38), including the use of zinc nitrate as an adjuvant in the reaction. In another process (39) nitration is effected with nitric acid in a chloroalkane such as methylene dichloride, the nitration mixture being regenerated by contact with a mixture of nitric and sulphuric acids.

Interest in the theory of cellulose nitration is directed to the accessibility of hydroxyl groups in cellulose to nitration and denitration. Yin & Brown (40) hold, on the basis of wetting and drying experiments at different temperatures, that their observation can best be explained in terms of the accessibility of primary rather than secondary hydroxyl groups. Dutch workers in a series of papers (41) have investigated the formation and denitration of cellulose nitrate. The two latest communications cover X-ray results on various samples, and describe concepts of the nitration equilibrium in terms of the accessibility of the hydroxyl groups.

The relative value of sulphate wood pulp, sulphite wood pulp, and linters for production of various propellants is recorded in a number of North American reports (42). Nitrated wood pulps, whether sulphate or sulphite, will meet 70% of American ordnance requirements, but are unsuitable for a number of rocket propellants owing to poorer physical properties and some indications of lower stability in accelerated heat tests. The function of the retained sulphuric acid in nitrocellulose stabilisation is still a subject of discussion. Thus Chedin (43) holds that steric occlusion is the correct hypothesis, and that there is no basis for the theory of ester formation. On the other hand, Millett *et al.* (44) conclude that the temperature coefficient of the stabilisation indicates that the rate-controlling step is a chemical reaction rather than a physical process.

A cold saline leach (45) followed by a short boil, beating and poaching, is of some value in stabilising pyrocellulose (12.6% N) but of little value for guncotton (13.4% N). Picatinny Arsenal workers also report on the effect of the stabilisation cycle on the life of propellants (46). Determination of the losses involved in the

kiering of nitrocellulose (47) may be performed by analysis of the liquor and the gases evolved.

One approach to the stabilisation question is to avoid the use of sulphuric acid: Spanish accounts discuss nitration and stabilisation under these conditions (48).

The removal of water from nitrocellulose can be accomplished by a continuous extraction process (49). Other patents describe the preparation of plasticisers with a boiling azeotrope of ethyl acetate, butyl acetate, methyl ethyl ketone or methyl isobutyl ketone (50), the grinding of nitrocellulose (51), and its preparation in convenient form for pouring (52).

Viscosity measurements on solutions are still being studied. Huque *et al.* (53), working on cellulose trinitrate, found an anomalous increase in viscosity per unit concentration in dilute solutions. Lhoste (54) found agreement between viscosities measured with a Hercules falling sphere viscometer and those measured by the French Service des Poudres method. It is suggested (55) that a higher degree of nitration increases the stiffness of the cellulose chain. Careful Dutch work (56) on solubility in alcohol-ether shows that the fall in solubility with increased nitrogen content occurs at 13.15% N at 20°, and at 13.20% N at 0°, but no connexion is indicated between these figures and the discontinuity of the (101) spacing at 13.15% N. The time dependance of the mechanical properties of a solution of nitrocellulose in diethyl phthalate has been reported upon (57).

The thermal decomposition of nitrocellulose has been studied by microwave examination of the products (58). The use of  $^{14}\text{C}$  (59) has shown that most of the glyoxal found on controlled ignition of cellulose nitrate derives from  $\text{C}_{(2)}$ , and an adjacent carbon of the anhydro-D-glucose unit.  $\text{C}_{(2)}$  and  $\text{C}_{(3)}$  provide some of the carbon dioxide and formic acid but very little of the formaldehyde.

The compounds of cellulose nitrate with acetone, camphor, and diphenyldiethylurea have been examined (60) by infra-red spectroscopy, and show evidence of hydrogen bonding to the carbonyl group of the plasticiser.

The nitration of carboxymethyl cellulose has been reported (61).

A number of methods of determining nitrogen in nitrocellulose are reported. In one method (62) the sample is dissolved in concentrated sulphuric acid and salicylic acid is added. Excess titanous chloride and back titration with ferric alum are used to estimate the nitrosalicylic acid formed. A modification of the known ferrous-titanous procedure (63) does not require full solution of the nitrocellulose before proceeding with the reduction by ferrous solution. With small samples of nitrocellulose (0.2-0.8 mg.) reaction with phenoldisulphonic acid, adjustment to pH 7.1-7.5, and reading of colour density at a wavelength of 400  $\mu\text{m}$  gives results to within 2% (64).

*Smokeless powder and ball powder*

Wasag patent (65*a*) a smokeless powder with dinitro- $\beta$ -phenylethyl nitrate instead of a more usual explosive oil. In a further publication (65*b*) a procedure is described for ensuring very fine division of the raw materials to obtain good mixing; in a supplement (65*c*) stabilisers are gelatinised in the nitroglycerine before it is added. Other improvements described include continuous feeding (65*d*).

In a series of patents, Olin Mathieson (66) describe treatment of smokeless powder grains with stannic oxide, di-isoalkyl phthalates of specified alcohols, or with lithium or barium nitrate. A low temperature coefficient is claimed for a powder surface-treated with certain polyol nitric esters (67).

Progressively burning powder is obtained by casting grains with a porous interior and dense exterior (68), or by distribution of high explosive through the grains. In a Dutch process the grain in ethanol is treated with phlegmatiser (69). Alternatively, it may be subjected to phlegmatisation and partial denitration (70).

The production of ball powder, or globular nitrocellulose, has been the subject of many patents by Olin Mathieson. Droplets of solution may be suspended in non-solvent (71*a*) in a continuous process, or nitrocellulose is suspended in a non-solvent and plasticiser added (71*b*); solvent is subsequently removed. Variants (71*c*) include production of particles less than 1/1000 in. in diameter, the use of protective colloids, the incorporation of water-soluble salts, and the making of ball powder with progressive burning properties.

Other patents (71*d*) describe the production of the size of powder grain required for different sizes of weapon. Other processes for making ball powder include agitation of nitrocellulose with a solvent under water, preferably hot (72). Ball powder is also produced in sizes below 100  $\mu$  diameter (73).

Analysis of ball powder for phthalate content may be performed by the hydroxamic colour procedure (74).

**Rocket propellants**

A number of review articles, conferences and books have shown the extent of activity taking place. A review by Johnson (75) discusses the merits of liquid propellants, monopropellants and solid propellants. More detailed information may be found in a bibliography (76) of about three hundred reports published by the U.S. Government. A number of books give recent data on rocket propellants (77). Other references are given in the Supplementary Bibliography.

No general classification of propellants can be made, but there

are two main groups: solid propellants and liquid propellants, whether monopropellants or bipropellants (see below).

Nuclear rockets have been the subject of calculations (78) and experiments have been described in which the specific impulse obtainable with accelerated plasma from exploding wires was measured (79): values much in excess of present chemical systems were obtained.

These systems are the responsibility of physicists and engineers. The chemist's hopes of improving impulse turn on ultra-energy fuels (80a) or on the use of free radicals and free atoms, but the main shortcoming of the latter is the limited concentrations achieved. Aerojet have taken notice of their possibilities (80b).

The cost and availability of rocket fuels and of oxidisers with particular reference to conditions in the United States have been summarised and discussed (81).

#### *Solid rocket propellants*

Solid propellants have advantages over liquids, e.g. in weapons which must be ready for instant use or which have to be transported without the possibility of constant skilled attention. The specific impulse of solid fillings has improved considerably over the years and figures of 240–250 sec. have been achieved; it is said that marginal improvements to 270 sec. are possible (82).

Most solid propellants are either classical propellants of double base type or consist of mixtures containing, essentially, an oxidiser and a fuel, which usually has binding properties (83) to give the required consistency to the propellant as a whole. The oxidant is almost always ammonium nitrate or ammonium perchlorate, but nitronium perchlorate has been suggested recently. The fuel binder may be one of many polymers. A solid propellant rocket motor with a controlled variation in thrust has been developed (84), which, if sufficiently versatile in application, would overcome a major drawback of solid propellant rockets. The mixing process is of primary importance in the processing of solid propellants.

The interest in the use of ammonium nitrate as an oxidant has led to work on its thermal decomposition (85) and its autocatalytic nature (86). The patent literature gives indication of the wide variety of fuels which may be used in conjunction with ammonium nitrate: an oxidisable metal and aluminium stearate (87); a rubber binder (88); a cellulose ester or polyvinyl acetate, together with plasticiser, catalyst and promoter (89).

The decomposition of ammonium perchlorate has also been studied. Galwey (90) finds that the mechanism of decomposition changes above 350°, above which temperature no residue remains.

The number of useful solid oxidants suitable for rocket propulsion is small. Nitronium perchlorate, with six oxygen atoms and one chlorine atom for each nitrogen is clearly well suited to

oxidising purposes, if its tendency to inflame organic materials on contact can be overcome (91).

Binder fuels for solid propellants are quite numerous and include polymerised hydrocarbons, depolymerised rubber, silicone rubber with an inorganic perchlorate oxidant, thermosetting resins, an alkyd-vinyl resin, polyformaldehyde and copolymers of 1,3-butadiene with 2-methyl-5-vinylpyridine optionally with styrene.

Among the more abstruse fuels, aminoborazanes deserve mention (92).

#### *Liquid rocket propellants*

Liquid rocket propellants fall into two main groups: monopropellants, in which oxidant and fuel are built into one molecule or in which the one forms a solution in the other, and bipropellants, in which two separate liquids are used at the time of firing. Particularly in the latter case, either fuel or oxidant or both may be cryogenic, and require cooling or insulation to maintain their liquid state until used. Cryogenic fuels include liquid hydrogen, while cryogenic oxidants include oxygen, ozone, nitric oxide, perchloryl fluoride and fluorine. Among the few manageable liquid oxidants are nitrogen tetroxide, nitric acid and hydrogen peroxide.

*Monopropellants.*—These excel in convenience and flexibility but fall behind in power, since separate oxidant fuel systems are less restricted as to sensitiveness requirements. Johnson (93) gives the following specific impulse figures for the more reasonable monopropellants consisting of single compounds.

Propellant	$\text{H}_2\text{O}_2$	90% Ethylene oxide	$\text{N}_2\text{H}_4$	Propyl nitrate	Nitromethane
Specific impulse	135	165	170	170	220

It will be seen that nitromethane is the most powerful of these.

A number of additives for use in monopropellants are described: for instance, 0.1–0.25% of nickel compounds in propyl nitrate (94) and dextran nitrate to produce a gel (95). The sensitivity to compression in contact with bubbles of some monopropellants, including  $\text{H}_2\text{O}_2$ , hydrazine, ethylene oxide, methylacetylene and propyl nitrate was investigated and analysed theoretically by Mead (96). The sensitivity of mixtures of nitrobody oxidant is sometimes high (97) and hazards arising in the use of 'Nisalit' (nitric acid acetonitrile) and 'Disalit' (nitric acid dimethyl ether) are described (98). Observations on the burning of a mixture of 2-nitropropane with nitric acid have been used to contribute to the theory of combustion kinetics (99).

*Bipropellants.*—The handling and thermodynamics of propellants, of the liquid hydrogen and liquid oxygen class in particular, were the subject of a conference, whose proceedings have now been published. Several papers in this volume deal with the handling of

liquid fluorine in tonnage quantities (100). Similar information is given for liquid hydrogen; other papers deal with boron propellants which are among the newer fuels.

Other fuels recommended include a eutectic of mono- and dimethylhydrazine (101), and a fuel containing both  $-NR_2$  and  $-SH$  groups (102). The liquid hydrazine decomposition flame has been discussed (103). The use of a fuel containing a major proportion of turpentine and up to 4.5% of lithium aluminium hydride, with a nitric acid oxidant, is envisaged (104). Among the oxidants Corelli describes the use of tetranitromethane, and compares it with others (105).

Theoretical calculations of the performance of JP 4 fuel (a hydrocarbon fuel) with mixtures of liquid ozone and fluorine have been published (106). A patent describes the use of fluorine-oxygen mixtures with gasoline, oxygen, triethylamine or other fuels (107).

### High explosives for civil use

#### *Ammonium nitrate*

Most innovations in this field are concerned with the use of ammonium nitrate, in particular in admixture with fuel oil.

There is a voluminous literature on ammonium nitrate, running to several hundred items. Among the issues of importance are the difficulties arising from the hygroscopic nature of ammonium nitrate, which causes caking, and its solubility, which means that special precautions are needed under wet conditions. Free-flowing or non-caking properties may be obtained by coating with powders, several formulations for which have been patented (see Supplementary Bibliography). Other difficulties arise from its relative insensitiveness as an explosive, which may be met by sensitising additions, by special boosters, and so on. Some applications are best handled by mixing the nitrate and fuel on site, although premixed materials have many advantages. Power per unit volume is a desideratum in some cases.

#### *Compounds containing nitro-groups*

A new type of safety explosive has been produced by Nitro-glycerin A.-B. consisting of compounds containing the trinitro-ethyl group. Urea or substituted ureas are reacted with formaldehyde and nitroform to produce compounds of the type of bis(trinitroethyl)urea (108).

The production of TNT from toluene gives a yield of  $\alpha$ -TNT below 90% even under the best conditions employed in industry. Part of the loss ( $\sim 4\%$ ) is due to *meta*-nitration and part to oxidation. The oxidation reaction was studied by Samuelson (109), who found that oxidation at the DNT stage occurs during nitration;

the oxidation of TNT, which is much less ionised than the DNT, may be avoided by control of the concentrations of nitric acid and water. A wide discussion of the whole subject of toluene nitration is given by Yamasue (110).

The detonation pressures achieved in liquid TNT are reported by Garn (111); the value of the plane steady-state amounts to 172 kilobars. The surprising report of Rinkenbach that molten TNT is nearly as sensitive as nitroglycerine is disputed by Urbanski (112), who finds it merely as sensitive as is picric acid at room temperature.

Japanese workers (113) have studied the effect of light on TNT. They find that visible light has none, but that the action of ultra-violet light is in two stages.

Analytical work related to TNT includes a tabulation of  $R_f$  values of various nitrated toluenes and benzenes in a chromatographic study (114), and a method of estimating DNT/TNT mixtures by non-aqueous titration (115) with tetrabutylammonium hydroxide in a mixed solvent.

Nitric acid solutions of various organic compounds have a long history as proposed explosives (116); among the compounds which have been examined for this purpose recently are nitrobenzene and *m*-nitrotoluene (117) and chloronitrobenzene (118).

The nitration of *N*-methyl-2,4,6-trinitraniline to give tetryl is shown to be a reaction of nitronium ion (119).

#### *RDX and other nitramines*

The path of carbon atoms in the nitrolysis of hexamine under conditions akin to those of the Combination Process has been traced by the use of carbon-14. Added paraformaldehyde is built into the final product on an equal footing with the methylene from the original hexamine, whether into RDX(cyclotrimethylene-trinitramine) or HMX(cyclotetramethylenetetranitramine) (120). The instability of solutions obtained by the nitrolysis of hexamine by concentrated nitric acid is due to the destabilising influence of nitrous acid present (121). The stabilisation of RDX waste acid can be achieved by autoclaving under prescribed conditions (122).

The casting of RDX-TNT mixtures and the viscosity changes of such mixtures have been described (123).

A number of methods of production of guanidine nitrate are described, e.g. by reaction of urea with ammonium nitrate (either reagent may be substituted) on a heated silica column (124), or of ammonium sulphamate with ammonia, sulphur dioxide and urea (125). The nitration of guanidine may be carried out in nitric acid, at a final concentration at least 93% nitric acid (126). The recovery of guanidine from mixtures with thiourea and ammonium thiocyanate is also described.

### Initiating explosives and detonators

There has been a considerable amount of activity in this field and many different types of compound have been tested and reported in the literature or patented. Prominent among initiators are metallic and organic acid azides, while delay compositions include oxidising agents such as red lead and barium peroxide with non-metallic elements such as silicon and selenium. References will be found in the Supplementary Bibliography.

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The following list includes only a few references from these journals, which will be accessible to specialists: *Mémorial des Poudres, Explosifs, Explosivstoffe, Sprengpraxis, Nobel Heft, Amer. Rocket Soc. J.*

### Propellant explosives

#### Nitrocellulose

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## FINE CHEMICALS AND MEDICINAL SUBSTANCES

By MEMBERS OF THE FINE CHEMICALS GROUP  
(Convenor: J. H. Chapman, Ph.D., F.R.I.C.)

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### Bacterial infections

THE new approach to the synthesis of penicillins made possible by the isolation in large quantities of 6-aminopenicillanic acid from fermentation liquors has been energetically exploited by the preparation of several hundreds of its derivatives (1, 2) in the search for more favourable absorption, a broader anti-microbial spectrum and reduced side-effects. The first of these, 6-( $\alpha$ -phenoxy-propionamido)penicillanic acid potassium salt (Broxil, phenethicillin), is an acid-resistant penicillin similar in its range of action to penicillins G and V and with possibly higher blood levels, although some workers have found a level of antibacterial activity in serum comparable with that of penicillin V (3-5). The higher *in vitro* resistance to staphylococcal penicillinase found in comparison with penicillins V and G suggested that Broxil might be useful in treating resistant staphylococcal infections, but this has not been supported by clinical experiment (6-8).

A more significant advance is represented by sodium 6-(2,6-dimethoxybenzamido)penicillanate monohydrate (BRL 1241, Celbenin), which has the remarkable property of complete resistance to staphylococcal penicillinase, an observation confirmed both in the laboratory and by clinical treatment of infections due to resistant staphylococci (9, 10), one of the most serious problems of antibacterial chemotherapy (11). Celbenin is, however, acid-sensitive and appreciably less active than penicillin G although secreted at the same rate; frequent injections are therefore necessary to maintain an effective blood-level. These factors and the relatively low activity against streptococci leave room for further improvement, although there is little doubt that Celbenin will be a valuable addition to anti-staphylococcal chemotherapy. Experience will show whether Celbenin-resistant strains of *Staphylococcus pyogenes*, similar to those already obtained by *in vitro* passage, emerge *in vivo* (12).



The incorporation of  $\alpha\omega$ -dicarboxylic acids as side-chains into the penicillin molecule by biosynthetic methods has shown that (4-carboxy-n-butyl)penicillin has similar activity to that of cephalosporin N, which contains an  $\alpha$ -aminoadipic side-chain (13). The total synthesis of nine new penicillins has been achieved, yielding in some cases enhanced resistance to penicillinase and to acid (14).

In the field of wide-spectrum antibiotics, demethylchlortetracycline, produced by a mutant of the organism used in chlor-tetracycline manufacture, appears to show enhanced activity over a wider range than tetracycline (15). Kanamycin has an activity comparable with that of tetracycline against *Pseudomonas* *in vitro* and slightly superior to it in other Gram-negative organisms (16).

Of the three newer sulphonamides included in last year's report, sulphaphenazole (Orisul) is well tolerated and has been found particularly useful in bacterial infections of the throat, respiratory tract and lungs (17). Sulphamethoxypyridazine (Lederkyn, Kynex) gave good results with streptomycin in non-gonococcal urethritis (18) and with chlortetracycline in male gonorrhoea (19); the sulphonamide has been associated with severe side-effects, but Canadian workers have concluded from a large number of cases that the incidence of cutaneous reactions is not unduly high (20). Sulphadimethoxine (Madribon) is almost completely absorbed from the intestinal tract and a concentration of up to 75% of the blood-level has been measured in cerebrospinal fluid (21).

The effect of protein-binding on the bacterial action of sulphonamides has been under investigation since 1943 (22) and evidence is now available that the albumin-bound fraction of a sulphonamide is devoid of antibacterial action. Several of the newer sulphonamides are more extensively bound to plasma-protein than sulphadimidine both in rabbits and in man, an observation which clearly suggests that higher plasma levels of such substances will be needed to produce an equivalent therapeutic effect (23).

Sulphasomizole (5-sulphanilamido-3-methylisothiazole) is a new antibacterial sulphonamide derived from the hitherto unknown isothiazole nucleus; *in vitro* and *in vivo* studies indicate a wide antibacterial spectrum, good absorption and distribution and an absence of crystalluria, but clinical studies have not yet been published (24).

2-Sulphanilamido-4,5-dimethylisoxazole (Sulfimox), a further new sulphonamide, appears to have activity *in vitro* equivalent to those of sulphadimidine, sulphamethoxypyridazine and sulphaphenazole. Maximal serum concentrations were obtained after 2 hours and binding to blood corpuscles was not observed; limited clinical experiments have shown good tolerance and ready passage into the cerebrospinal fluid (25). Amongst other sulphonamides currently under investigation are 2-sulphanilamido-5-methylpyrimidine

(Pallidin) (26), 2-sulphanilamido-5-methylisoxazole (sulphisomazole, sulphamethoxazole) (27), and azosulphonamides such as 2,6-diamino-3-phenylazopyridine sulphatriazine salt (28).

### Virus diseases

New work on interferon, the protein nature of which now seems to be confirmed, has recently been reviewed (29). Some *in vivo* testing has been possible; interferon derived from rabbit kidney cells and applied externally to the eyes of rabbits after corneal inoculation of vaccinia virus delayed and suppressed symptoms of infection, but there was no effect in an ocular herpes simplex infection (30).

A systematic study (31) of compounds related to isatin 3-thiosemicarbazone, shown in 1953 to be active against vaccinia virus, has indicated that the overall dimensions of this molecule appear to be nearly optimal since substitution of the benzene ring and changes in the position or character of the side-chain invariably led to reduced activity (against neurotropic vaccinia in mice). 1-Ethylisatin 3-thiosemicarbazone, however, showed enhanced activity in this test and protected mice against the effects of alastrim virus when injected after infection, the high therapeutic index suggesting possible applications to human smallpox (32).

The antiviral activity of certain glyoxals has been further explored in a series of diphenyl keto-aldehydes and related substances. *p*-( $\alpha$ -Ethoxy-*p*-phenylphenacylamido)benzoic acid in particular showed considerable activity against influenza virus in mice and against canine distemper; it has given encouraging results in the oral treatment of human herpes virus infections (33).

*N,N*-Anhydrobis-(3-hydroxyethyl)biguanide hydrochloride (ABOB) showed some suppressive effect in the course of a double-blind trial during an epidemic of influenza A, and evidence of prophylaxis was subsequently obtained using an association (Flumidin) of ABOB with atropine methonitrate and scopolamine methonitrate. Confirmation of these results and further developments will be awaited with interest (34).

### Tuberculosis and leprosy

The drug treatment of tuberculosis both by 'standard chemotherapy' with streptomycin, isoniazid and *p*-aminosalicylic acid salts and by newer agents in the case of bacilli resistant to these three has been reviewed by Crofton (35). The status of one of the more promising new drugs,  $\alpha$ -ethylisonicotinic thioamide (ethionamide, Trescatyl), has been the subject of a recent survey (36) in the light of the preliminary findings of the Clinical Trials Committee of the B.T.A. Research Committee (37). When given in association either with pyrazinamide or with cycloserine the drug

produced negative sputa (for at least one month) in about one-third of advanced pulmonary cases which had not responded to 'standard' treatment. Some gastric intolerance has been noted in this and in other clinical trials where good therapeutic results in 'resistant' cases were obtained (38).

Ethyl dithiol-terephthalate and -isophthalate (ditophal, Etisul), previously shown to have antitubercular activity in mice, have been tested in guinea-pigs (39). Both were active, but less so than was streptomycin, in a subcutaneous infection; only ditophal was active in an intracerebral infection, but less so than isoniazid. Topical application of ditophal gave some improvement in cases of cutaneous tuberculosis (40).

Blocking the primary hydroxyl group of dihydrostreptomycin resulted in a diminution of activity, thus supporting the hypothesis that microbiological oxidation to streptomycin is essential for activity in the former substance (41).

Considerable anti-tubercular activity in guinea-pigs is claimed for a water-soluble peptide derivative, polymethyl- $\alpha$ -poly-L-glutamate (Polyanthin) (42).

Isonicotinoyl-3,4-diethoxybenzylidenehydrazone suppressed murine leprosy when given shortly after infection, but acid-fast bacilli did not disappear from the site of inoculation in advanced leprosy mice although the healing of lesions was observed (43). 4-Butoxy-4'-dimethylaminodiphenylthiourea (Su 1906) proved effective in four cases of lepromatous leprosy resistant to sulphone treatment (44). The current status of the therapy of leprosy has been recently reviewed (45). For the treatment of the lepra reaction, which occurs frequently during sulphone therapy, chloroquine has been found useful (46).

### Amoebiasis

Earlier work has shown that dichloroacet-4-hydroxy-N-methyl-anilide (diloxanide, Entamide), which is relatively ineffective in acute amoebic dysentery, is absorbed rather easily from the gastrointestinal tract. Attempts to modify this characteristic have led to the benzoate and furoate, which are less well absorbed, and to the piperazine sulphate, which is better absorbed. The furoate, which shows by far the highest *in vitro* activity of these compounds, also appears to be the most clinically promising in the treatment both of cyst-passers and, especially at higher dosage-rates (30 mg. kg. day for 10 days), of acute cases (47). It is not clear whether this enhanced effectiveness is due to inherently greater activity or its poorer absorption in the gastro-intestinal tract, resulting in a higher colonic concentration. The significance of the relapse rate recorded in these trials has been discussed (48).

Dichloroacetamides have been the subject of further patents (49) and chlorbetamide (Mantomide, Pontalin) has received further,

rather unsuccessful, clinical evaluation, only 50% clearance being achieved in chronic cases (50).

Paromomycin (Humatin) is an antibiotic with high activity *in vitro* against *Entamoeba histolytica* and a favourable therapeutic index in rats and dogs. Significant activity, particularly by the subcutaneous route, is also claimed in amoebic hepatitis of the hamster (51). Clinically, the drug was effective in chronic infections but ulcers were rather slow to heal and the relapse rate was higher than encountered during standard treatment with emetine bismuth iodide (52).

No drug has yet emerged to replace emetine with chloroquine, or chloroquine alone in the presence of cardiovascular disease, for the treatment of amoebic liver abscess (53). Some of the difficulties involved in establishing a laboratory test for the evaluation of compounds in this aspect of amoebiasis have been discussed (54).

### Trypanosomiasis

Studies on the absorption, distribution and secretion of 2-amino-7-(2-amino-6-methylpyrimidin-4-ylamino)-9-*p*-aminophenylphenanthridine 10,1'-dimethobromide (prothidium) in rats, rabbits and cattle have shown that the prophylactic action of this drug in cattle is probably due to the formation of a depot at the site of injection (55). In a comparison of the prophylaxis against bovine trypanosomiasis achieved by metamidium chloride, the suramin salt of metamidium (M & B 4427), prothidium and quinapyramine prophylactic, the mean duration of protection against a high level of natural challenge was significantly greater with the fine suspension of M & B 4427 than with any of the other drugs. The superiority of the suramin salt over the metamidium chloride may have been due to the physical state of the injection rather than to any difference in the amount of active cation given. A strong local reaction at the site of injection was observed with both preparations of metamidium (56).

Following an earlier trial in which nitrofurazone was successfully used in human cases of *T. gambiense* resistant to other treatment, this drug has been given preliminary trial in resistant or relapsed *T. rhodesiense* cases. Consistent response was not obtained but the drug showed sufficient promise in a small number of cases to warrant fuller investigation (57).

A further trial on 11 cases of *T. gambiense* with pentylthiarsaphenylmelamine (Mel W), a water-soluble form of the melarsen oxide/BAL complex (Mel B), has confirmed the earlier favourable view (see last year's Report) of this injectable product. Success was also reported in two cases complicated by onchocerciasis, one of whom received the drug together with antimony  $\alpha\alpha$ -dimercapto-succinate (58).

### Other protozoal diseases

The idea that mass chemotherapy in the control of malaria may be practicable as a local substitute for insecticide application has prompted a limited trial of a tablet combination of amodiaquin (150 mg.) and primaquine (15 mg.) in *Plasmodium vivax* infection. Both protective and curative effects were claimed (59). The instability of primaquine phosphate under normal conditions of usage as a salt additive has been reported (60). A closely related drug, 6-methoxy-8-(4-aminopentylamino)quinoline (Quinocide) may have a useful place in the treatment and prophylaxis of vivax malaria since it destroys the tissue stages of the parasite (61). 4,4'-Diaminodiphenyl sulphone (Dapsone) is active against both *P. malariae* and *P. falciparum*, but slower in effect than chloroquine and possibly not so completely suppressive (62). A series of  $N^1$ -aryl- $N^2$ -amidine ureas has been tested against *P. gallinaceum* in chicks and two (aryl =  $p$ - $\text{NO}_2\text{C}_6\text{H}_4$  and  $p$ - $\text{NH}_2\text{C}_6\text{H}_4$  respectively) proved active (63).

Last year's Report referred to preliminary results in the systemic treatment of *Trichomonas vaginalis* infections with 1-5-hydroxy-ethyl-2-methyl-5-nitroimidazole (metronidazole, Flagyl). Extensive clinical experience has now confirmed that this is a major therapeutic advance. Trichomonal vaginitis is comparatively widespread and treatment by topically applied drugs has never been entirely satisfactory. Further, there is now evidence that transmission of the protozoan to males is a likely cause of reinfection; concurrent treatment of male and female is thus very desirable and is practicable only by means of a systemically effective drug. Earlier attempts to use 2-acetamido-5-nitrothiazole systemically were disappointing, but there is every indication that metronidazole is successful in a high proportion of cases, male and female, by oral administration. Apparent failure may be due to reinfection, or to inability to absorb the drug, and it is only in the latter cases that local use of the drug seems necessary (64).

A series of 1-(2-alkyl-4-amino-5-pyrimidinylmethyl)alkylpyridinium salts, and of analogous 3-thiazolium compounds, have been investigated for prophylactic action in coccidiosis, a poultry disease caused by *Eimeria tenella* and related protozoa. These compounds, of which 1-(4-amino-2-n-propyl-5-pyrimidinylmethyl)-2-picolinium chloride hydrochloride (amprolium) is the most useful, appear to act by a reversible inhibition of thiamine, since addition of the latter substance to the diet causes a significant decrease in the protection afforded (65).

*Babesia divergens* is the causal organism of British bovine red-water (babesiosis), commonly treated with quinuronium sulphate or with the less toxic, but less effective, 4,4'-diaminodiazaoamino-benzene (Berenil) and other amidines. A new drug, 3,3'-diamidino-

carbanilide di-isethionate (amicarbalide), has emerged by screening against *B. rodhaini* in mice and *B. divergens* in calves, and has given satisfactory results in a field trial in 90 cattle (66).

### Helminthiasis

The evaluation of antimony compounds in schistosomiasis continues. The response to Triostam (trivalent sodium antimony gluconate), given by injection to cases of double infection by *Schistosoma haematobium* and *S. mansoni*, was less good in the latter than in the former parasite (67). Further work with antimony  $\alpha\alpha$ -dimercaptosuccinate has shown that the earlier encouraging results with urinary bilharziasis cannot necessarily be applied to the intestinal disease (68). Chinese work with Sb-11 (see previous Report) and with an antimony complex of 8-hydroxyquinoline indicates that the latter may be superior and less toxic than tartar emetic in experimental infections in mice (69).

Conflicting results, possibly due to different dosage and clinical material, have been obtained in comparisons between bephenium (benzyltrimethyl-2-phenoxyethylammonium) salts and tetrachloroethylene in hookworm infestations (70). The value of bephenium hydroxynaphthoate (Mecpar) in ascariasis has been confirmed, as has its relatively poorer activity in trichuriasis (71). Dithiazanine (3,3'-diethylthiadicarbocyanine iodide), which is claimed to have 'broad spectrum' anthelmintic activity, has been further evaluated in the mass treatment of various intestinal helminths (72) and a modified formulation is said to have improved the rather poor tolerance of this substance without any change in efficacy against enterobiasis (73).

Favourable preliminary results were obtained in tests with 2-thienylmethyl 2-imidazolyl sulphide hydrochloride against *Nematostrioides dubius* in mice (74).

A safer and more effective agent than carbon tetrachloride and hexachloroethane against *Fasciola hepatica*, the common liver fluke of sheep, is still required; tetrachlorodifluoroethane has comparatively low toxicity and was highly effective in mature flukes, but variable in its effect on immature flukes. Further trials will be carried out (75).

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## NEUROMUSCULAR BLOCKING AGENTS

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STEADY interest has been maintained in neuromuscular blocking agents over the past five years and the volume of new work reported is so great that a complete bibliography cannot be given in the limited space available. Studies on the mode of action of these agents have continued to appear and a very significant advance has been the attempt to place their classification on a more rational footing (*1*).

In the following a chemical classification has been largely adopted and studies which are of biological importance or involve structure-action relationships are indicated in the text when considered necessary.

### Naturally occurring substances

#### *Alkaloids and alkaloidal derivatives*

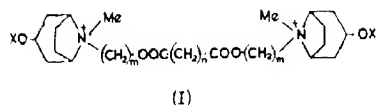
In 1959, Waser & Harbeck (*2*) reported the first clinical use of toxiferine-1 and curarine-1, and Waser (*3*) has also demonstrated the distribution of curarine-<sup>14</sup>C in the mouse diaphragm by auto-

radiographic techniques. Muscle-relaxant activity has been reported in alkaloids, etc., from various plants (4-15).

Quaternary ammonium derivatives of strychnine and strychnine *N*-oxide have been studied (16); of these, the pentamethylene bis-strychninium derivative was four times as potent and half as toxic as tubocurarine. Studies have been made of the curare-like alkaloids of Brazilian *Strychnos* sp. (17) and of the tertiary amine dihydro- $\beta$ -erythroidine, the mechanism of action of which resembles that of tubocurarine (18, 19). McIntyre lists several alkaloids isolated from *Erythrina* sp. and recently *E. falcata* was reported to contain curare-like alkaloids (20).

Maltoxin, an amine obtained from brewer's malt rootlets, is reported to cause a depolarising block in the frog (21).

Bis-tropinium derivatives with the formula (I), (R=phenyl-acetyl,  $n = 4$ ,  $m = 2$ , is the most satisfactory compound), have



muscle-relaxant properties (22). hexamethylene bis-atropinium and bis-scopolinium derivatives are muscle relaxants, but retain the anti-muscarinic activity of the parent alkaloids (23). In a series of polymethylenebis-diethyl-(7-theophylline ethyl)ammonium bromides, curarising potency increases as the number of methylene groups increases up to 10 (24). Some polymethylenebis-(1-ethyl-theobromine)ammonium bromides also possess curarising activity (25).

#### Antibiotics

Neomycin sulphate was reported to be the cause of four cases of apnoea (two fatal) (26). Neomycin has tubocurarine-like activity in animals and ether increases its effects (27-29). Streptomycin and tetracycline also cause neuromuscular block, the former and neomycin resembling magnesium (30-32).

#### Vitamins

Thiamine, pyridoxamine, oxythiamine, acetylthiamine and co-carboxylase in large doses cause neuromuscular and ganglion block in the rat and dog (33-35). Thiamine block has been reported to be reversed by neostigmine (34) but other workers do not confirm this (35). Pantothenic acid has been reported to prolong and increase the effects of tubocurarine in man (36).

*Naturally occurring choline esters, etc.*

Murexine (urocanoylcholine;  $\beta$ -imidazol-4-ylacrylcholine) is a suxamethonium-like depolarising neuromuscular blocking agent (37-39) which is hydrolysed by cholinesterase (40). Other murexine-like substances have also been investigated (41-45). Leptodactyline [(*m*-hydroxyphenylethyl)trimethylammonium], a phenylalkylamine extracted from the skin of *Leptodactylus ocellatus* and *L. pentadactylus*, possesses both nicotinic and neuromuscular blocking activity (46).

Interest has also been shown in the paralysing properties of tetrodotoxin, a poison isolated from the roe of the globe fish (47, 48), and in shell fish poisons (49, 50).

### Synthetic compounds

*Aliphatic and aryl-aliphatic onium salts*

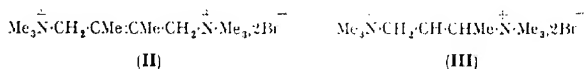
Tetraethylammonium (TEA) has continued to arouse experimental interest; thus kitten diaphragm is reported to be more sensitive to TEA than that of rat, guinea pig or rabbit. TEA has been shown to act directly on muscle fibres and to increase acetylcholine release at nerve endings.  $\beta$ -Hydroxy-TEA possessed TEA-like properties (51, 52).

*Decamethonium and some allied compounds*

Decamethonium has now been shown to possess a dual mode of action and this is of considerable interest in view of earlier studies (53). Decamethonium dioxide is devoid of neuromuscular blocking activity (54) and it is clear that the presence of one or two ether oxygens in straight-chain bis- and tris-onium compounds sharply reduces potency (55). The low potency of the 4-C member of the polymethylenebis-(trimethylammonium) series is said to be due to increased interaction between the charged onium atoms as inter-onium distance shortens, so that the 2- and 3-C analogues may act as single, doubly charged ions (56).

Amongst other polymethylenebis-ammonium derivatives, decamethylenebis(trimethylammonium) methosulphate and decamethylenebis(dimethylbenzylammonium) chloride have potent neuromuscular blocking activity in cat, rabbit, rat and frog (54).

Compounds (II) and (III) have neuromuscular blocking and



parasympathomimetic properties (57). Ethylene bis(dodecynyl-dimethylammonium) chloride is also reported (58), while 1,10-bis-(dimethylamino)cyclo-octadecane dimethiodide (59) has tubo-

curarine-like relaxant activity and cyclo-octadecane both ganglion and neuromuscular blocking activity.

Studies of *NS*-bis-, *NNN*-tris-, *NSN*-tris-, *NNNN*-tetra-, *NNSNN*-penta- and *NNNNNN*-hexa-onium salts to gain information on the receptor surface at the neuromuscular synapse and to correlate structure with activity have also appeared (60).

#### *Aliphatic bis-onium ethers*

A series of muscle-relaxant bis-quaternary ethers most of which are aliphatic or aryl-aliphatic and derived from  $R(C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot NMe_3I^+)_2$  has been synthesised (61). A German patent (62) describes muscle-relaxant quaternary triamines and an East German patent (63) the dimethiodides of succinic acid mono- $\beta$ -dimethylaminoethyl ester, mono- $\beta$ -dimethylaminoethyl methylamide and the corresponding benzylamide. Of interest is the description of muscle-relaxant properties in some quaternary ammonium polymers made from alkyl vinyl ethers (64). Ganglion blocking and neuromuscular blocking activity have been found in quaternary alkyl ethers (65). Prodeconium[diohexadecanium; *NNN'N'*-tetramethyl-*NN'*-bis(propoxycarbonylmethyl)-3,14-diohexadecane-1,16-diammonium bromide] possesses two ether and two ester-linkages and has been used clinically as a short-acting relaxant (66). It produces a mixed block more closely related to tubocurarine than decamethonium.

#### *Aliphatic bis-onium esters*

Carbamic acid esters of the general formula  $RR'N \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot NEt_3X^+$  ( $R, R' = H, Et, Ph, 2-C_{10}H_7$  or  $\beta-C_4H_9 \cdot OC_6H_4$ ;  $R' = H, Et$  or  $Ph$ ;  $X = Cl$  or  $I$ ) have muscle-relaxant activity (67). A series of polymethylene bis-(carbamoylcholine) chlorides [general formula  $NN(CH_3)_3^+(CH_2)_2 \cdot NH \cdot CO \cdot O \cdot (CH_2)_n \cdot O \cdot CO \cdot NH \cdot (CH_2)_2 \cdot N^+(CH_3)_3$ , where  $n = 2, 6, 9$  or  $10$  and  $X = Cl$  or  $I$ ] are also reported (68). In this series Imbretil [hexamethylenebis(carbamoylcholine)] bromide has been used clinically and is approximately equipotent with tubocurarine.

#### *Suxamethonium*

Cases of prolonged apnoea following suxamethonium are due to pseudocholinesterase deficiency and these coupled with the resemblance of suxamethonium to acetylcholine have led to studies on suxamethonium-enzyme interactions (68a). Further light on the mode of action of depolarising relaxants has been thrown by a comparison of the actions of suxamethonium, tubocurarine and decamethonium on chicken muscle and on the muscle of new-born kittens (69). Suxamethonium, benzoquinonium, neostigmine and

decamethonium but not gallamine or tubocurarine reduce twitch tension in directly stimulated muscle (70). Muscle pain after suxamethonium can be diminished by tubocurarine (71) or if the former is replaced by suxaethonium (72).

A group of dicholine esters of dicarboxylic acids related to suxamethonium are described in an East European publication and evidence of East European interest in the properties of suxamethonium is clear (73). A series of *NN'*-bis-( $\omega$ -dialkylaminoalkyl)-amides of dibasic aliphatic acids quaternised with benzyl halides has also yielded neuromuscular blocking agents (74).

#### *Aromatic derivatives*

*p*-Phenylenebis(acetylcholine), some *p*-phenylene diacetates, *p*-alkoxyphenylacetates, *p*-hydroxyphenylpropionates, *o*-homophthalates and *p*-homophthalates (74), and the quaternary salts of ethylalkylamine ethers derived from hydroxy- and dihydroxydiphenyl sulphones, possess muscle-relaxant activity (75). Some *p*-xylenebis(ammonium) salts cause ganglion blockade and respiratory paralysis in dogs (76), while neuromuscular blocking activity is reported in bis-quaternary phthaloyl esters (77) and in the triethirdide of bis(diethylaminoethyl) 4-dimethylaminoisophthalate (78), in benzyltrimethyl ammonium iodide, in a series of substituted benzyltrimethylammonium iodides and in furfuryltrimethylammonium iodide (79). Condensation of platynecine with 1,3-bis(bromoethoxy)benzene gives 1,3-bis-(*p*-platynecineethoxy)-benzene, which is reported to have relaxant activity (80). There are patent specifications referring to quaternary salts of aniline ethers (81) and to aryl- and aralkyl-bis(triphenylphosphonium) salts (82).

A series of 4,4'-diacetophenone derivatives with quaternary ammonium or pyridinium groups substituted symmetrically in the  $\alpha\alpha'$ -positions possess neuromuscular blocking and anticholinesterase activity. Compounds with a hydroxyethyl group on the quaternary nitrogen atom apparently form derivatives containing quasi-six-membered rings through an inter-reaction between the hydroxyethyl and carbonyl groups, and these were called hemicholiniums. Hemicholinium No. 3 [ $\alpha\alpha'$ -bis(dimethylethanolamino)-4,4'-diacetophenone] is a muscle relaxant with a slow onset but prolonged action (83).

Benzoquinonium [2,5-bis-(3-ethylaminopropylamino)benzoquinone bis(benzyl chloride)] has a 'mixed' action resembling tubocurarine more closely than decamethonium: it has been used clinically (84). The properties of 2,5-bis-(3-hexamethyleniminopropylamino)-*p*-benzoquinone have also been described (85), and (1,4-diacetoxy-2-methylnaphthyl)benzyl-diethylammonium is reported to possess action similar to that of TEA (86).

Hexafluorenium [hexamethylene-1,6-bis-(9-fluorenyldimethylammonium) dibromide], a weak tubocurarine-like relaxant syn-

thesised by Cavallito and his co-workers (87), has been investigated in dogs by Macri (88), and clinical reports have appeared (89). It is an anti-cholinesterase and prolongs and delays the onset of action of suxamethonium or suxaethonium (90). Bronchoconstriction has been reported to follow the combined use of hexafluorenum and suxamethonium (91).

#### *Heterocyclic derivatives*

Neuromuscular blocking activity has been reported in 1-[3-(4-methyl-1-piperaziny)propyl]-3,3-diphenylpyrrolidine-2,5-dione, its hydrochloride and methiodide (92), a series of  $N^1N^3$ -disubstituted barbiturates (93), 3,6-bis-(tertiary-aminoalkyl)pyridazines (94), dimethylaminoethyl 5-ethoxymethylfuran-2-carboxylate methiodide (95), and substituted aminoalkylhydrazines and their salts (96). The synthesis and properties of pentamethylene-bis-( $N$ -methylpyrrolidinium) and 3,6-bis-[2-(1-methyl-1-pyrrolidinium)-ethoxy]pyridazine di-iodide have also been reported (97).

2,2'-Dodecamethylenebis-( $N,N'$ -dimethylpiperidinium) iodide is a short-acting, muscle relaxant about equipotent with tubocurarine (98). 'Mixed' muscle-relaxant activity has been found in bis-(3-hydroxydimethylpiperidinium) bromide ethers with 5-8, 10, 12 or 14 methylene groups (99). 2-Diethylaminoethoxyethyl  $\alpha$ -phenyl- $\alpha$ -piperididhoacetate dimethiodide is a short-acting, tubocurarine-like relaxant with a rapid onset of effect (100). The properties of a series of dimethiodides of  $\alpha$ -phenyl- $\alpha$ -tertiary-amino acetates of  $\beta$ -tertiary-aminoethoxyethanol have also been described (101).

Neuromuscular blocking activity has also been found in the piperidino-, morpholino-, hexamethyleneamino-, diethylamino-, and dimethylamino-derivatives of some  $\omega\omega'$ -diaminodibutyl ether dimethiodides (102).

#### *Chlorpromazine*

There is some agreement that chlorpromazine augments the actions of tubocurarine but decreases those of depolarising drugs (although there is a report that chlorpromazine increases the actions of both tubocurarine and suxamethonium on rat diaphragm preparations). Not all investigators agree that it has tubocurarine-like properties of its own (103).

#### *Drug interactions*

Triphenylmethane dyestuffs which have no muscle-relaxant activity potentiate tubocurarine (104). Other dyes, e.g. Congo red, Trypan blue, Trypan red and Germanin, form insoluble complexes *in vitro* with tubocurarine, but suxamethonium forms no complex with Congo red. The view is expressed that formation *in vitro* of a precipitate is not related to the anti-curare action *in vivo* (105). The anti-curare action of these dyestuffs was referred to by Ferrari



& Costa, but Kensler was of the opinion that complex formation was responsible for the anti-curare activity (106). Germanin does not relieve suxamethonium-induced muscle pain in man (107).

Chlorothiazide increases tubocurarine activity (108) but galanthamine antagonises tubocurarine (109), diphenhydramine and promethazine antagonise TEA but potentiate gallamine (110). Other tubocurarine antagonists reported include tetrahydroamin-acrine, which also antagonises gallamine (111), phenolphthalein (112), and 2-formyl-1-methylpyrrolidinium iodide oxime, which also intensifies the actions of suxamethonium and decamethonium (113). Harmine and belladonna increase the effects of suxamethonium (114), but apomorphine, homatropine, co-carboxylase, thiamine disulphide, 4-aminopyrine and tubocurarine antagonise them. Chlorpromazine and bulbo-capnine had no such effect (114).

Intra-arterial histamine antagonises the depolarising but potentiates the non-depolarising relaxants (115). Sodium L-thyroxine increases sensitivity to decamethonium and neostigmine but not to suxamethonium or tubocurarine (116), and 2,4-dinitrophenol can cause neuromuscular blockade (117). Guanidine reverses the actions of depolarising drugs yet increases acetylcholine release per impulse from the nerve endings (118). TEA restores neuromuscular transmission in the partially curarised kitten, rabbit and rat, an effect thought due to increased acetylcholine release (119). *d*-Amphetamine and tetrahydro- $\beta$ -naphthylamine reduce the rabbit head-drop dose of tubocurarine (120).

Succinylbis(sulphocholine) is antagonised by trimethylsulphonium, TEA, hexamethonium and hexamethylenebis(methylsulphonium) (121).

Certain sulphonamides potentiate tubocurarine (122). 21-Hydroxypregnanedione potentiates laudexium but antagonises decamethonium (123) and meprobamate increases the toxicity of tubocurarine (124). Carbon dioxide antagonises suxamethonium, decamethonium and gallamine but increases the activity of tubocurarine (125) and mecamlamine (126). Mecamlamine and trimetaphan camphorsulphonate given prior to hexamethonium produce neuromuscular block (127). Hexamethonium, trimetaphan and homatropenium can themselves cause block but are more effective after preliminary curarisation (128).

## Conclusion

The neuromuscular blocking agents that are in current and extensive clinical use are the non-depolarising drugs tubocurarine and gallamine and the depolarising compound suxamethonium. All three were introduced more than five years ago, all have disadvantages in clinical use, yet so far none has been satisfactorily replaced. This in itself is perhaps a sufficient commentary on the

difficulty of the task and the measure of success achieved in the period reviewed. Tubocurarine has a long duration of action, it possesses ganglion-blocking activity and may release histamine. Gallamine is somewhat shorter acting, but paralyses the cardiac vagus, while suxamethonium, a short-acting drug, causes initial muscular twitching and fibrillation which may lead to post-operative muscular soreness and stiffness. In rare instances it may cause prolonged apnoea and unlike tubocurarine and gallamine it has no clinical antidote—a serious disadvantage. All three compounds can however be used with safety and give satisfactory results. Tubocurarine and gallamine are now so well tried that it would be difficult to introduce substitutes unless these possess quite exceptional properties, but a short-acting, non-depolarising drug with no trace of 'mixed' activity to replace suxamethonium is desirable, and this appears to be a profitable avenue for research. It has to be emphasised that 'mixed'-acting drugs are likely to be unsuccessful in practice because they may exhibit varying degrees of irreversibility in patients.

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**DEPRESSANTS AND STIMULANTS OF THE CENTRAL NERVOUS SYSTEM** (R. Howe, B.Sc., Ph.D., A.R.I.C., & E. H. P. Young, M.Sc., Ph.D.)

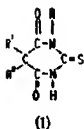
*Imperial Chemical Industries Ltd., Pharmaceuticals Division*

**Volatile anaesthetics**

2-Bromo-2-chloro-1,1,1-trifluoroethane (Halothane, Fluothane) has now proved to be a safe and efficient inhalation anaesthetic for all types of surgery and has an extensive literature (1). The pharmacokinetics of Halothane anaesthesia has been reported (2) and the pharmacology reviewed (3). Tritium-labelled Halothane has been prepared (4). The central depressant effect of Halothane is reported to be reduced by the use of the Halothane-ether azeotrope (5). Interest in fluorinated hydrocarbons (6) and fluorinated ethers (7) has continued. 2,2-Dichloro-1,1-difluoroethyl methyl ether (Methoxyflurane) has been successful in a limited clinical trial (8). The induction was smooth and emergence was without delirium or hypotension and with decreased nausea. It is non-flammable.

**Intravenous anaesthetics**

The synthesis and resolution of 5-allyl-1-methyl-5-(1-methyl-2-pentynyl)barbituric acid (Compound 25,398, Lilly) (Methohexital, Brevital) has been described (9) and further confirmation of its clinical value as an ultra-short-acting barbiturate reported (10). Further variations in the side chains of thiopentone (I,  $R=H$ ,  $R'=MeCH_2\cdot CH_2\cdot CHMe$ ,  $R''=Et$ ) to produce a short-acting thiobarbiturate have been reported (11); B137 ( $R=Me$ ,  $R'=Et$ ,  $R''=Me_2CH\cdot CH_2$ ) is on clinical trial.



The potent analgesic 1-(1-phenylcyclohexyl)piperidine (Sernyl, CI-395 Parke Davis) (12) and the related compounds *N*-ethyl-1-phenylcyclohexylamine (Cyclohexamin, CI-400) and 1-(1-2'-thienylcyclohexyl)piperidine (CI-421) have been used as intravenous anaesthetics for minor surgery (13). The anaesthetic effect was reported to be good, with little disturbance of respiration or circulation. Lack of muscular relaxation was a disadvantage.

Several oxetanes have shown anaesthetic activity in rats, accompanied by considerable toxicity (14). The best, 3,3-diethyl-oxotane (15), which is related to the anticonvulsant Prenderol (16), also showed sedative and anticonvulsant activity.

The sodium hemisuccinate of 21-hydroxypregnane-3,20-dione (Viadriol, Roche Products; Presuren, Schering A.G.), first introduced by Murphy *et al.* (17), has proved useful as an intravenous anaesthetic (18).



### Anticonvulsants

The types of drugs now available for the treatment of epilepsies have been reviewed (19). The possible clinical usefulness of monoamine oxidase inhibitors in epilepsy is under investigation (20).

In the cyclic amide class of anticonvulsants, results with 1-phenyl-5,5-diethylbarbituric acid (Pyrietal, B.W. No. 401) against febrile seizures have been sufficiently encouraging to warrant further evaluation (21). The promise shown by neopentylallylbarbituric acid (Nevental, A.B. Pharmacia) in animal experiments has not been fulfilled clinically (22). The pharmacology and structure-activity relationships of a series of urazoles having a nucleus isosteric with that of the hydantoins has been discussed (23).  $\alpha$ -(*p*-Aminophenyl)- $\alpha$ -ethylglutarimide (Elipten, CIBA), an analogue of the hypnotic Doriden ( $\alpha$ -ethyl- $\alpha$ -phenylglutarimide), has been reported to be a useful adjunct in the management of epileptics (24).

In small trials, the carbonic anhydrase inhibitor 6-ethoxybenzothiazole-2-sulphonamide (Ethoxzolamide, Cardrase) has been shown to control both *grand mal* and *petit mal* seizures (25). Interest in the anticonvulsant activity of quinazolones (26), including the hypnotic 2-methyl-3-*o*-tolyl-4-(3H)-quinazolinone (Tuazolone, Tuazole) has recently developed, but clinical evidence is not yet available. The most active compound of those tested by the British Drug Houses was 2-methyl-3-*p*-bromophenyl-4-(3H)-quinazolinone hydrochloride (B.D.H. 1880).

### Hypnotics

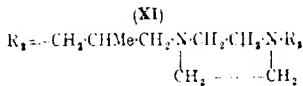
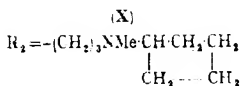
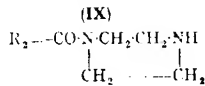
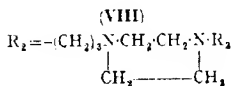
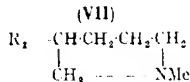
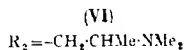
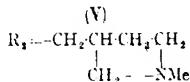
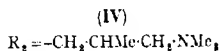
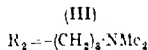
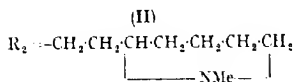
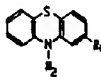
New barbiturate-type hypnotics continue to appear. One of these, 5-allyl-1-methyl-5-(1-methyl-2-pentynyl)barbituric acid, has been separated into its four optically active isomers (9, 27). Striking pharmacological differences were noted between the isomers. A similar compound, 5-allyl-5-neopentylbarbituric acid (Nevental) (28), has been tried clinically (29) and it is claimed to have a rapid action and is not followed by tiredness or drowsiness. The properties of another related allylbarbituric acid, 5-allyl-5-*s*-butylbarbituric acid (talbutol), have recently been described (30). The variation in distribution of the various barbituric acids is dependent upon both the mass of the 5,5-substituents and the inductive effect of these substituents on the hydrophilic part of the molecule (31). Similar effects have been noted in a related series of aza-uracils (32). A new synthesis of thiobarbituric acids, which were evaluated as brief-acting hypnotics, has been described (33). Several glutarimides have been recommended as substitutes for barbiturates which are potentially dangerous drugs. Glutethimide,  $\alpha$ -ethyl- $\alpha$ -phenylglutarimide, is not without danger at high dosage (34). One of the safest and most effective non-barbiturate hypnotics is

*N*-phthaloylglutamic acid imide (Distaval, Contergan) (35), whose pharmacological actions have now been described (36). Other related cyclic imides which have been prepared include some 2,2-disubstituted-thiomorpholine-3,5-diones (37), 3,3-dialkylpiperazine-2,6-diones (38), 4-alkylpiperazine-2,6-diones (39), and azetidine-2,4-diones (40). The Italian workers who prepared the azetidinones also prepared some 3,3-disubstituted-2-azetidinones and 3,3-disubstituted azetidines (41), some of which in the course of pharmacological investigation showed marked sedative and hypnotic properties (42). The glutarimides, particularly glutethimide, are said to differ from all other barbituric and non-barbituric sedatives in their ability to inhibit cholinergic pathways (43). Another new hypnotic which is a cyclic amide is 2-methyl-3-*o*-tolyl-4-(3H)-quinazolone (TR495; Tuazole) (44), which has been examined by Ravina (45) and found to be clinically effective and to have few side effects. Further work has been reported on acetylenic carbinols and glycols and their respective carbamates. Methylpentynyl carbamate has been described as being a safe and effective hypnotic in geriatric cases (46) and a favourable clinical trial of 2-methyl-2-*s*-butylpropane-1,3-diol dicarbamate (W.583) has been reported (47). Some 2,2-dialkylpropane-1,3-diol bis-(alkoxyalkylcarbamates) showed no meprobamate-like activity (48). Ethinamate (1-ethynylcyclohexylcarbamate) is metabolised to 1-ethynyl-4-hydroxycyclohexylcarbamate (49). It has been shown that the acetylenic bond is essential for high activity in a series of cyclic carbinols (50). The carbamates of some bicyclic ethynyl carbinols were also active (51). Replacement of the ethynyl group by a propargyl group in both the carbinol and the carbamate series (52) has yielded active compounds, the best being 1-propargylcyclohexyl carbamate (Merimax) (53). The effect of variations in the size of the ring, the nature of the urethane grouping and other ring substituents have been investigated (54). An entirely different chemical type is represented by 3,4,5-trimethoxybenzoyl-glycine-*NN*-diethylamide (trimeglamide), which has been tried successfully in man (55). A number of related glycineamides has been prepared (56) and a closely related compound *N*-(3,4,5-trimethoxybenzoyl)tetrahydro-1,4-oxazine (Trioxan, Compound V-7) (57) is now in clinical use. Yet another new type of compound, 2-*o*-hydroxy-1,3,4-oxadiazole (Hypnazol) has hypnotic properties and has been used successfully in the treatment of insomnia (58). In a series of ureides prepared from ethyl 4-phenylpiperidine-4-carboxylate and substituted ureas, the compound derived from *N*-ethylurea was found to be hypnotic (59).

### Tranquillisers

Along with the discovery of new phenothiazines an enormous amount of information is amassing concerning the mode of action,

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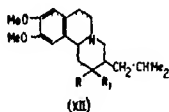


KS75 (II,  $R_1 = \text{OC}_3\text{H}_7$ ) (62, 63), TZ11 (III,  $R_1 = \text{SMe}$ ) (61, 62), SKF6270 (IV,  $R_1 = \text{SMe}$ ) (64), SKF7535-A (IV,  $R_1 = \text{CF}_3$ ) (65), methidiazine (Tacaryl, V,  $R_1 = \text{H}$ ) (66), ethylisobutrazine (Sergélyi 6484 R.P., Diquel, VI,  $R_1 = \text{Et}$ ) (67), propiomazine (Propavan, VI,  $R_1 = \text{COEt}$ ) (68), P1030 (VII,  $R_1 = \text{OMe}$ ) (69), pipamazine (Mornidine, VIII,  $R_1 = \text{Cl}$ ,  $R_3 = \text{CONH}_2$ ) (70), Sch. 6673 (VIII,  $R_1 = \text{Ac}$ ,  $R_3 = \text{CH}_2\text{-CH}_2\text{-OH}$ ) (71), fluphenazine (Permitil, Prolixin, VIII,  $R_1 = \text{CF}_3$ ,  $R_3 = \text{CH}_2\text{-CH}_2\text{-OH}$ ) (72), perazin (Taxilan, PT25, VIII,  $R_1 = \text{H}$ ,  $R_3 = \text{Me}$ ) (73), trifluoperazine (Stelazine, VIII,  $R_1 = \text{CF}_3$ ,  $R_3 = \text{Me}$ ) (74), 5501 MD (IX,  $R_1 = \text{H}$ ) (75), CIBA 17,040 (X,  $R_1 = \text{Cl}$ ) (76), 6710 R.P. (XI,  $R_1 = \text{Cl}$ ,  $R_3 = \text{Me}$ ) (77), and 7843 R.P. (VIII,  $R_1 = \text{SO}_2\text{-NMe}_2$ ,  $R_3 = \text{Me}$ ) (78). Much new clinical and pharmacological information has been published on the following established phenothiazines: perphenazine (Trilafon, VIII,  $R_1 = \text{Cl}$ ,  $R_3 = \text{-CH}_2\text{-CH}_2\text{-OH}$ ) (79), thiopropazate (Dartal, VIII,  $R_1 = \text{Cl}$ ,  $R_3 = \text{-CH}_2\text{-CH}_2\text{-OAc}$ ) (80), prochlorperazine (Stémétil, VIII,  $R_1 = \text{Cl}$ ,  $R_3 = \text{Me}$ ) (81), methopromazine (Mopazine, III,  $R_1 = \text{OMe}$ ) (82),

and triflupromazine (Vesprin, **III**,  $R_1 = CF_3$ ) (83). Numerous cases of jaundice, agranulocytosis and extrapyramidal side effects have been reported (84). Increase in potency has often been achieved at the expense of increased toxicity and comparative studies have been undertaken to determine which is the best drug of this class (85). The preparation of several of these phenothiazines and related compounds has been described (86). One related compound, chlorprothixen,  $\alpha$ -2-chloro-9-(3'-dimethylaminopropylidene)thioxanthone (Taractan, Truxol) has recently been introduced. Clinical reports state that it has marked antidepressant activity in addition to being a tranquilliser (87). Related thioxanthenes and thioxanthene-S-oxides have also been studied (88).

The novel compound 7-chloro-2-methylamino-5-phenyl-3H-1,4-benzodiazepine-4-oxide hydrochloride (methaminodiazepoxide, Librium) (89) has interesting tranquillising properties which include specific anti-aggressive effects. Its unusual pharmacological properties (90), and preliminary clinical results (91) have been disclosed. Minor side effects have been noted (92).

Favourable clinical results (93) have been obtained with another new chemical type of tranquilliser, 3-isobutyl-1,2,3,4,6,7-hexahydro-9,10-dimethoxy-2-oxobenz-(a)-quinolizine (tetrabenazine,



Nitoman, **XII**,  $R + R_1 = O$ ). It does not have the side effects of reserpine (which it antagonises), probably because it acts solely on brain-amines and has little influence on peripheral physiological amines. In other respects it behaves like a short-acting reserpine (94). The pharma-

cological properties of two related 2-substituted benzquinolizines in which  $R = OH$  and  $R_1 = Et$  and  $(CH_2)_2CH(OMe) \cdot CH_3$  (**XII**) respectively have been reported (95). Analogues of reserpine and chemically simpler compounds based on its structure continue to be prepared and tested (96). Central nervous depressant activity was found in some indolylethylpyridines, which potentiated the anaesthetic action of barbiturates and antagonised the effects of the amphetamine group of central nervous system stimulants. Clinical trials in agitated patients have been encouraging and side effects are few (97). Many carbamates related to meprobamate have been tested. Melander (98) examined a series of tertiary alcohols and esters and found 1-ethyl-1-methylpropyl carbamate (emyclate, Nuncital) to be clinically twice as active as meprobamate (99). 3-Hydroxy-2-phenylethyl carbamate (styramate, Sinaxar) (100) is also more depressant than meprobamate.

Good clinical results (101) with few side effects have been claimed for 1-*m*-aminophenyl-2-pyridone (amphenidone, Dornwal), the pharmacological properties of which are also known (102). An anti-inflammatory compound, 3-phenylpropyl carbamate (pro-

formiphen, Gamaquil) has muscle-relaxant and tranquillising properties (103).

Neuroplegic properties were exhibited by several amides and ureides of 2-alkylcrotonic acids (104) and also by some alkoxybenzamides (105). A clinically effective amide which resembles meprobamate in its action is 2-ethyl-3-propylglycidamide (oxanamide, Quiactin) (106). The synthesis of this and several closely related compounds has been described (107). Different chemical types for which sedative action is claimed include 2,2-disubstituted dioxans (108), 1,3-dioxolans and 1,3-dioxans (109), 2-oxazolines (110), benz-1,4-dioxans (111), 5,5-disubstituted-1,3-oxazine-2,4-diones (112), oxazolidinediones (113), 5-aryloxymethyl-2-oxazolidinones (114) and some guanamines (115).

### Central stimulants

Interest in central stimulants has centred upon monoamine-oxidase inhibitors, mainly derivatives of hydrazine. The first of these was 1-isonicotinyl-2-isopropylhydrazine (iproniazid, Marsalid), which aroused great clinical interest (116). Several similar compounds which have since been used clinically are: 2-phenylethylhydrazine (phenelzine, Nardil) (117), 2-phenylisopropylhydrazine (JB516, Catron, Cavodil) (118), 1-benzyl-2-(5-methyl-3-isoxazolylcarbonyl)hydrazine (isocarboxazid, Marplan) (119) and 1-isonicotinyl-2-(3-benzylcarbamylethyl)hydrazine (nialamide, Niamid) (120). The clinical effects and pharmacological side effects of these and related hydrazines have been summarised (121). Non-hydrazine stimulants which inhibit monoamine-oxidase are *trans*-2-phenylcyclopropylamine hydrochloride (tranylcypromine, SKF385, Parnate), which has had a clinical trial (122), *N*-benzyl-*N*-methyl-2-propynylamine hydrochloride (A 19,120) (123), harmaline (124) and  $\alpha$ -ethyltryptamine (Monase) (125).

The compound *N*-(3-dimethylaminopropyl)-iminodibenzyl (imipramine, Tofranil), which causes mood elevation by a depressant action on the central nervous system (126), is one of the most valuable drugs available for the treatment of depression. Much information is now available concerning its clinical effectiveness (127), pharmacology (128), metabolism (129), toxicology (130) and preparation (131).

The clinical value of methyl phenyl- $\alpha$ -piperidylacetate (methylphenidate, Ritalin) in the treatment of depression has been challenged. It is said by some workers to be no better than a placebo (132), whilst others claim that it is a useful drug (133). The synthesis of *dl*- and the optical isomers of  $\alpha$ -3-thiamorpholinylbenzhydrol (134) and esters of 2-piperidylphenylmethanol (135), which are related to methylphenidate and pipradrol (Meratran), has been described. Stimulant activity has been found in a series

of oxazolidinediones (136), amides of *d*- $\alpha$ -methylphenylethylamine (137), diphenylmethylpseudothiureas (138), dialkylaminoalkyl derivatives of theophylline (139) and some 5,5-disubstituted barbituric acids (140).

8-Aminomethyl derivatives of 7-hydroxy-chromones and -flavones were found to be powerful brain-stem stimulants similar in action to strychnine (141). Convulsant central nervous stimulation was also exhibited by some bicyclic sulphonium salts (142), 1-isobornyl-5-alkyltetrazoles (143), monohalogenated derivatives of sulpholane (144) and 5,7-diphenyl-1,3-diaza-adamant-6-ol (1757 I.S.) (145).

### Psychotomimetic agents

This term is being used to group together drugs which mimic the psychoses and should be accepted with reservation until the relationship between a model and a real psychosis has been clarified (146). Psilocybin is a recent notable addition to this group of which the most familiar members are lysergic diethylamide (L.S.D.) and mescaline. Psilocybin, the psychotropic principle of the mushroom *Psilocybe mexicana* Heim, was isolated by Hofmann *et al.* (147), who also determined and confirmed its structure by synthesis as the phosphoric ester of *N,N*-dimethyl-4-hydroxytryptamine (148). Psilocin, the non-phosphorylated analogue of psilocybin, possesses similar pharmacological and psychotic properties. Other analogues have been prepared (149) and the history and pharmacology of psilocybin reviewed (150). Small doses of the drug produce changes in mood and in contact with the environment, while higher doses produce changes in orientation and cause development of psycho-sensory phenomena. Delay *et al.* (151) have reported a therapeutic effect in a compulsion neurosis, but clinically the drug is in its infancy.

A number of substituted glycollic acid esters of *N*-alkyl-3-piperidols having anticholinergic activity (152) have recently been demonstrated to possess psychotomimetic properties (153). *N*-Ethyl-3-piperidyl cyclopentylphenylglycollate (JB329) was said to have clinical effects which simulated some aspects of psychosis more closely than L.S.D. or mescaline. 1,2,3,4-Tetrahydro-5-amino-acridone (Tetrahydroaminacrin), a cholinesterase inhibitor, was an effective antidote to model psychoses induced by JB329 (154).

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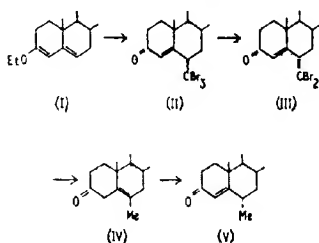
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### STEROID HORMONES (V. Petrow, Ph.D., D.Sc., F.R.I.C.)

*The British Drug Houses Ltd.*

LAST year attention was drawn to the American practice of omitting physical and/or physicochemical data characteristic of compounds which form the subject of product patents. A similar practice is now apparent in patents issued in this country. Thus a recent specification emanating from abroad describes two examples of a method of preparation of steroidal products. No melting points or other physical characteristics are given. The specific product claims, however, embrace no fewer than 16 compounds and their functional derivatives. The danger to industrial interests inherent in this development is too self-evident to require comment.

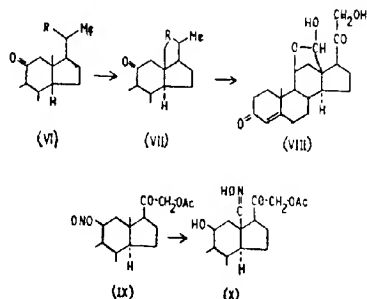
The most interesting advance in the year under review has undoubtedly been the application of free-radical reactions to the production of steroidal materials. Thus the Leo Company of Copenhagen, a newcomer to the steroid field, has described the application of a free-radical addition reaction to the preparation of the commercially important 6-methylated steroidal hormones (I). A 3-oxo- $\Delta^4$ -steroid was converted into the 3-enol ether (II).



Reaction of the last compound with carbon tetrabromide in collidine led to 1,4-addition of  $\text{Br}$  and  $\text{CBr}_3$  with elimination of ethyl bromide and formation of the 6 $\beta$ -tribromomethyl ketone (II). Reaction with pyridine gave the dibromomethylene ketone (III), converted by catalytic hydrogenation into (IV) and thence by treatment with  $\text{H}^+$  or  $\text{OH}^-$  into (V). The method was successfully

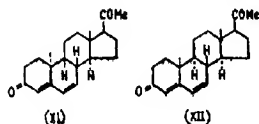
applied to the preparation of the potent progestational agent 17 $\alpha$ -acetoxy-6 $\alpha$ -methylprogesterone and to 6 $\alpha$ -methylcortisone.

Free-radical reactions have also been successfully applied to the preparation of aldosterone. 3 $\alpha$ -Hydroxy-5 $\alpha$ -pregnane-3,20-dione was converted into the 20-methylamino-derivative (VI; R = NHMe). The corresponding chlorimine (VI; R = NMeCl) underwent



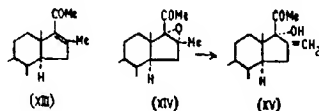
the Loeffler-Freytag reaction on irradiation to yield the 18,20-methylamine (VII; R = NHMe) transformed by conventional reactions into aldosterone (VIII) (2). A simpler route to (VIII) involved lead tetra-acetate oxidation of 3 $\alpha$ -acetoxy-20 $\alpha$ -hydroxy-5 $\beta$ -pregnan-11-one (VI; R =  $\alpha$ -OH) to the 18,20-epoxide (VII; R = O) and thence to (VIII) (3). A combined Anglo-American team has described the direct conversion of corticosterone acetate 11-nitrite (IX) into aldosterone acetate oxime (X) by photolysis in benzene under nitrogen and thence by reaction with NaNO<sub>2</sub>/acetic acid into (VIII) (4).

The search for new modifications of the steroidal structure has led to the preparation of 9 $\beta$ ,10 $\alpha$ -progesterone by the degradation of lumisterol<sub>3</sub>. The novel isomer of progesterone was converted into various 9 $\beta$ ,10 $\alpha$ -analogues of steroidal hormones, one of which, 9 $\beta$ ,10 $\alpha$ -pregna-4,6-diene-3,20-dione (XI), proved to be considerably more potent as a progestational agent than the corresponding pregna-4,6-diene-3,20-dione (XII) (5) of 'natural' stereochemistry about C<sub>9</sub> and C<sub>10</sub>. The discovery of other highly active compounds of 'unnatural' stereochemistry about C<sub>9</sub> and C<sub>10</sub> may confidently be expected.





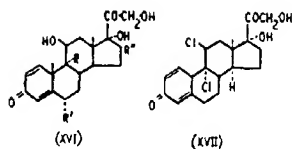
Work on a 17 $\alpha$ -hydroxy-16 $\alpha$ -methylpregnan-20-one has unexpectedly led to the discovery of the 17 $\alpha$ -hydroxy-16-methylenepregnan-20-one group of hormones (XV). The readily available 16-methylpregn-16-en-20-ones (XIII) were treated with hydrogen



peroxide under alkaline conditions, when the corresponding 16 $\alpha$ ,17 $\alpha$ -epoxides (XIV) were obtained. Reaction of these compounds with mineral acids led to smooth formation of the 17 $\alpha$ -hydroxy-16-methylenepregnan-20-ones (XV) (6). Application of this reaction to several types of hormones has been described (see below).

#### *Anti-inflammatory steroids*

Study of the methylated and halogenated derivatives of prednisolone and 9 $\alpha$ -fluoroprednisolone has continued. With the discovery of the potentiating effect upon anti-inflammatory activity of 6 $\alpha$ - and 16 $\alpha$ - (and 16 $\beta$ -) methylation, it was to be expected that the disubstituted 6 $\alpha$ ,16 $\alpha$ -dimethylated corticoids would be prepared. This has now been achieved by two different teams, and the products obtained (XVI; R=H or F, R'=Me, R''=-H, --Me) have the expected high order of activity (7). The 6 $\alpha$ -fluorinated



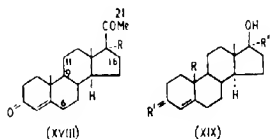
derivative of triamcinolone (XVI; R=R'=F, R''=-H, --OH) (8) and of 9 $\alpha$ -fluoro-16 $\alpha$ -methylprednisolone (XVI; R=R'=F, R''=-H, --Me) (9) have also been prepared by conventional methods, as has the 6 $\alpha$ -methyl derivative of 16 $\alpha$ -hydroxyprednisolone (XVI; R=H, R'=Me, R''=-H, --OH) (10). All these compounds considerably exceed prednisolone in anti-inflammatory activity and are reported to be without sodium-retaining properties.

New mono-substituted derivatives of prednisolone (and its 9 $\alpha$ -fluoro derivative) which show promise include the 21-methyl- (11), 16 $\alpha$ -fluoro- (12), 16 $\beta$ -fluoro- (13) and 16-methylene-derivatives (14). The 9 $\alpha$ ,11 $\beta$ -dihalo- and, in particular, the 9 $\alpha$ ,11 $\beta$ -dichloro-steroid (XVII), although biologically less active than

prednisolone (15) by the systemic route, is reported to show excellent topical activity in allergic skin conditions (16). A 21-deoxy-corticoid, 9 $\alpha$ -fluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-6 $\alpha$ -methylpregna-1,4-diene-3,20-dione, is claimed to be a highly potent anti-inflammatory agent when applied topically (17). Not one of the known corticoids, however, may be described as a pure anti-inflammatory substance. All of them show a whole spectrum of biological activities including undesirable inhibitory effects upon the adrenals, enhancement of infective processes, etc., so that the search for better compounds will continue.

#### Progestational agents

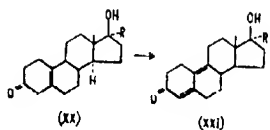
Broadly speaking, the most important progestational types are those derived from progesterone (XVIII; R=H), testosterone (XIX; R=Me, R'=O, R''=H) and 19-nortestosterone (XX; R=H, R'=O, R''=H).



Simple derivatives of progesterone which have been described during the past year include 6 $\alpha$ ,16 $\alpha$ -dimethylprogesterone (18) and its 6-dehydro-derivative (19), 17 $\alpha$ -bromo-6 $\alpha$ -fluoroprogesterone (20), 6 $\alpha$ -chloro-17 $\alpha$ -chloro(bromo)progesterone (21), and 9 $\alpha$ ,11 $\beta$ -dichloroprogesterone (22). These compounds, however, show only a fraction of the progestational activity of the substituted 17 $\alpha$ -acetoxy derivatives of progesterone (XVIII; R=OAc) such as 17 $\alpha$ -acetoxy-6-methyl-6-dehydroprogesterone (23), 17 $\alpha$ -acetoxy-21-fluoro-6 $\alpha$ -methylprogesterone (24) and 17 $\alpha$ -acetoxy-6 $\alpha$ -methyl-16-methyleneprogesterone (25).

Interest in 17 $\alpha$ -substituted derivatives of testosterone has continued, and 17 $\alpha$ -allyloestr-4-en-17 $\beta$ -ol (XX; R=H, R'=H<sub>2</sub>, R''=CH<sub>2</sub>CH:CH<sub>2</sub>) has been reported to show good progestational potency without concomitant androgenicity (26).

By treating the 17 $\alpha$ -substituted oestr-5(10)-en-3-one (XX) with bromine in pyridine solution, a new series of progestational agents (XXI) has been obtained. Some of these, e.g. (XXI; R=C:CH),

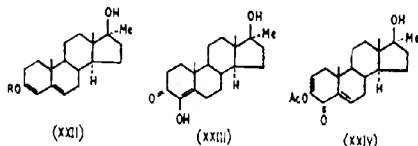


reduce fecundity in the rat (27). The word 'claudogen' (derived from claudere=to halt) has been proposed for steroids with anti-fertility properties (28).

The possibility that progestational agents may be effective against neoplasms was adumbrated some 25 years ago [Lipschutz (29)]. 17 $\alpha$ -Acetoxy-9 $\alpha$ -fluoro-11 $\beta$ -hydroxy-6 $\alpha$ -methylpregna-1,4-diene-3,20-dione has now been found to be effective against a C3-H mammary adenocarcinoma in mice and against a testosterone propionate-resistant fibroadenoma in rats (30). Further developments may be expected with confidence.

#### *Anabolic/androgenic agents*

Conversion of 17 $\alpha$ -methyltestosterone into a series of enol ethers (XXII) and particularly into the cyclohexyl enol ether (XXII; R=C<sub>6</sub>H<sub>11</sub>) has been reported. The latter compound is five times more active than the parent ketone as an androgenic/anabolic agent when administered by the oral route (31), but shows only slight activity on subcutaneous administration. 4-Hydroxy-17 $\alpha$ -methyltestosterone (XXIII) (32) and 3-acetoxy-17 $\beta$ -hydroxy-17 $\alpha$ -methylandrosta-2,5-dien-3-one (XXIV) (33) represent other interesting compounds of this type.



#### *Other biologically active types*

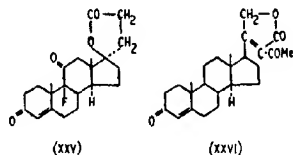
The novel spirolactone (XXV) is reported to have marked anti-DOCA properties (34). 9 $\alpha$ -Fluoro-DOCA, in contrast, exceeds deoxycorticosterone in sodium-retaining potency by a factor of 12 (35).

Many substituted derivatives and analogues of the oestrogens have been examined for hypocholesteremic activity (36). 16,16-Difluoro-oestrone 3-methyl ether appears to be outstandingly active (37).

The search for sedatives and tranquillisers of the steroid type has continued with moderate success (38). The most important advantage that steroidal compounds may be expected to possess over heterocyclic drugs is a freedom from toxic effects on chronic administration. A major advance in this field would undoubtedly have wide repercussions.

Pregnenolone derivatives containing basic substituents at C<sub>(16)</sub>

have shown promise as coronary dilators (39) and cardiac anti-accelerating agents (40). The synthetic butenolide (XXVI), pre-



pared by the action of diketene on deoxycorticosterone, appears to be as active as digitoxin in the isolated rabbit heart preparation (41).

Steroids with antifungal (42), antiandrogenic (43) and anti-cortisone properties (44) have been obtained.

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## RADIATION PROTECTIVE AGENTS

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In 1949, Bacq & Herve (1) and Patt *et al.* (2) found that an injection of cyanide or cysteine respectively enabled a mouse to survive an otherwise lethal dose of X-rays. Since that time this subject has expanded rapidly and a bibliography of several hundred references could easily be compiled. Fortunately it is dealt with in great detail in two recent books (3, 4) to which the reader is referred for the literature.

Several hundred substances are now known which reduce the biological damage from ionising radiations at all levels ranging from isolated cells to intact animals. For a substance to be called a protective agent it has to be effective if given before the irradiation (usually not more than 20 minutes before); measures that are taken after irradiation are not protection, but treatment.

The protective agents are usually most effective against sparsely ionising radiations such as X- (and  $\gamma$ -) rays, and high-energy electrons. Radiations in which the energy is not deposited in a more or less random manner but as densely ionised tracks such as  $\alpha$ -particles (or the protons from fast neutrons) can be protected against to a much smaller extent. The best way of expressing the extent of protection is as a dose reduction factor which is defined as dose required to produce a given effect (such as to kill one-half, LD<sub>50</sub>) when the organism is protected, divided by the dose needed to produce the same result in an unprotected organism.

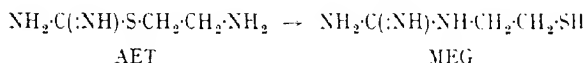
Protective agents have generally been studied with mammals, and in a typical experiment 100% protection can be obtained; e.g., 800r of X-rays will kill ten out of ten mice (the actual dose depends to some extent on the strain used) within 15 days, but if the mice are given an injection of a good protective agent before irradiation all the animals will be alive several months afterwards. The actual dose reduction factor required to obtain this result need however only be 1.5 since the dose response curve for killing by ionising radiations is very steep, so that a dose of 550r would not kill any of these mice acutely (i.e., within 30 days). The most effective of the protective agents give a dose reduction factor of up to 2.5 for mice, although their effectiveness is less in rats and dogs. The few experiments that have been performed with monkeys indicate that primates can be protected. To obtain a significant degree of protection, all the substances that have so far been discovered have to be given in amounts which come close to giving pharmacological side-effects. While the activity of the different substances when expressed as mg./kg. varies very greatly, these



differences are much smaller when their 'therapeutic index' is compared.

The acute effects of radiation (such as death within 30 days) are the consequence of the killing of cells at critical sites such as the bone marrow and the intestine. Protection occurs by reducing the fraction of cells that are killed by the radiation. Experiments with micro-organisms and insects have shown that chemical protection against some of the genetic effects (e.g., induction of mutations) is also possible. There is, however, no clear-cut evidence that the same chemicals protect irradiated mammals against the late somatic effects such as the induction of cancers, leukaemia and cataracts, or the shortening of life span.

The most active protectors are compounds which contain a sulphhydryl group and a basic group (amino or guanidino) separated by not more than three carbon atoms, i.e.,  $\text{SH}\cdot\text{C}\cdot\text{C}\cdot\text{N}<$ . Cysteine and glutathione, but not homocysteine, are amongst the best protectors. Loss of the carboxyl function greatly raises the activity (i.e., lowers the dose needed) and cysteamine,  $\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , has become the parent substance of a large group of active substances. Of particular interest is aminoethylthiourea (AET), which rearranges rapidly under physiological conditions to give the highly active substance, mercaptoethylguanidine (MEG).



Amongst other sulphur-containing compounds, ammonium di-thiocarbamate and alkyl derivatives (e.g., *NN*-diethylthiocarbamate) are highly active. Substitution on the sulphur atom led to loss of protective action. Cystamine ( $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ ) is particularly useful in mice since it protects even one hour after its administration, while cysteamine is virtually ineffective half an hour after injection. A moderate degree of protection is obtained with anaesthetics, tranquillisers and pharmacologically active amines such as histamines, all of which are believed to protect by reducing the oxygen tension in animals. Serotonin (5-hydroxy-tryptamine) protects very well, but the evidence is conflicting whether anoxia is involved. Cyanide and nitriles protect some animals but not others and they may work by anoxia, although this has not been definitely proved. Alcohols can give a small degree of protection in mammals, but they protect bacteria extremely well.

Many investigations into the mechanism of action of the most effective substances (i.e., those containing SH groups) have been carried out, but the question is still unanswered. Depletion of oxygen has sometimes been noted in protected animals, but this

cannot in general explain their effectiveness. Since protectors have to be present during the irradiation, it seems likely that they function by reacting with the short-lived radiation-induced radicals (either from water or from organic substances) which initiate the chain of events that leads to cell death. But the exact nature of the primary chemical processes in radiobiology is not known and discussion of the chemical reactions involved in protection are therefore highly speculative.

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### NEWER TECHNIQUES OF PURIFICATION

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#### *Isolation and purification of proteins and other charged substances of high molecular weight*

FOLLOWING the remarkable success of ion-exchange techniques as tools for the separation of small organic ions, it was natural to expect that a concerted attack would be made on the problem of extending their use to the potentially more important field of biological macromolecules. There were, however, a number of difficulties in doing this. Ion-exchange resins depend for their success on the rapid diffusion of the organic ions into and out of the particles of resin gel. This rate of diffusion may be influenced by variations in temperature, particle size, on the degree of cross-linking of the resin substance, but even with a very lightly cross-linked resin there is a precise limit to molecular size above which a solute can no longer penetrate.

It is clear, therefore, that if macromolecular substances are to be separated, the process of adsorption and desorption must be carried on at the surface of the resin particles, and if any multi-plate or chromatographic process is to be attempted desorption must be rapid and complete. Generally the ion-exchange resins, having bead form or smooth-fractured surfaces, present only a small surface area to contact with the solute and the adsorption of macromolecules by such resins is usually too small to be of value in technical separations. A first step in the solution of the problem

was taken when it was found that the resin Amberlite IRC-50 exhibited a high reversible capacity for proteins. This resin is a carboxylic cation-exchanger based on polymethacrylic acid and probably owes its high absorption capacity for macromolecules to the extensively sintered surface of the particles. With finely powdered IRC-50, the basic proteins cytochrome *c* (1), lysozyme (2) and ribonuclease (3) were eluted from columns as very sharp peaks by buffer solutions in the range pH 7-8 and were recovered quantitatively.

The same resin has since been used for technical-scale purification of large basic peptides and for some basic proteins which resist denaturation on surfaces, but since the lower limit of dissociation of the resin carboxyl group is about pH 5.5 the range of application of the resin as a true ion-exchanger is limited. The unexpected observation was made (4), however, that, unlike the amino-acids, many neutral proteins were adsorbed by the resin below pH 6 when the resin carboxyl groups are largely undissociated. This effect could be used to extend the range of application to neutral proteins such as the haemoglobins (4, 5) but conditions were not found for the reversible adsorption of acidic proteins.

It is usually found that, when dealing with proteins or other biological macromolecules, the separation procedures are very critically dependent upon control of pH and ionic strength of the buffer solutions. A serious disadvantage in the use of polymethacrylic acid resins lies in their high exchange capacity for inorganic ions. This results in a high buffering capacity and corresponding difficulties in pH control when using a succession of buffers for elution. In an attempt to avoid this difficulty, and to extend the range of application to acidic proteins, Boardman (6) studied a resin made by coating the surface of a diatomaceous earth with a thin layer of sulphonated polystyrene (7). This offered a large surface with negligible buffering capacity and the resin was successfully used for the purification of insulin (8).

#### *Use of ion-exchange reagents based on cellulose*

A new approach to the problem was made when in 1956 Peterson & Sober (9) introduced ion-exchange reagents based on cellulose. The hydroxyl groups of cellulose may be substituted by a variety of radicles with an acidic or basic function and the degree of substitution may be controlled within fairly wide limits. It was found that ion-exchange reagents which possessed a high capacity for macromolecular ions could be made by substituting only a few of the available hydroxyl groups, and because of the low degree of substitution the reagents have a low buffering capacity. A sample of diethylaminoethyl (DEAE)-cellulose had an exchange capacity for inorganic anions of only 1 mequiv. per g. but adsorbed 75% of its own weight of bovine serum albumin at pH 7 from solution in

0.01M phosphate buffer. Carboxymethyl (CM)-cellulose had a similarly low exchange capacity for inorganic cations and adsorbed its own weight of haemoglobin from dilute phosphate buffer at pH 6.0. In both cases the protein could be recovered quantitatively by elution with a suitable buffer.

From the moment of their introduction, the cellulose ion-exchangers began to show their value over a rapidly widening field of application. In analytical separations a chromatographic technique using either a pH gradient or a concentration gradient was commonly employed and many elegant separations have been reported. Serum albumin (10) was fractionated on DEAE-cellulose with a gradient of decreasing pH and increasing salt concentration. Fractions containing solely  $\beta$ -globulins,  $\gamma$ -globulins or albumin were obtained, but certain other fractions were electrophoretically complex. Nitrogen recovery was substantially complete and useful separations were obtained with loads as high as 170 mg. per g. of adsorbent.

The nucleic acids are families of closely related polyanions of very high molecular weight which have hitherto been difficult to separate and characterise. Successful fractionation of the native substances and products of mild degradation using ECTEOLA-cellulose has now been reported (11). Simple nucleotides have been separated and purified by the same reagent (12) and oligonucleotides have been successfully chromatographed with DEAE-cellulose (13). Similarly, the use of DEAE-cellulose for the isolation of proteolytic enzymes from pancreatic juice has proved valuable. With a column 70 cm. long and a concentration gradient of phosphate buffer at pH 8.0, eight anionic protein components were separated from one another (14). Six of these were identified as carboxypeptidase-B, procarboxypeptidase-B, chymotrypsinogen-B, deoxyribonuclease and the two forms of procarboxypeptidase-A.

These three examples may be sufficient to illustrate the high degree of resolution obtainable with cellulose ion-exchangers and the diverse classes of macromolecular substances which have already yielded to their use. Other examples are given in the Supplementary Bibliography.

#### *Separations on a larger scale*

In practical separations with macromolecular substances it is often observed that a strictly chromatographic procedure is unnecessary and that good separations can be obtained by using the column simply as an adsorption filter. In this technique the mixture to be separated is applied to the column as a buffer solution from which it is freely adsorbed and the components are then displaced one at a time by washing with a series of buffers of increasing eluting power. This observation is in apparent contradiction to all previous experience in the chromatography of small ions and arises

from the 'all or nothing' character of the distribution of macromolecules between two phases. It can be shown from thermodynamic considerations (15) that in general when a macromolecular substance is distributed between two phases, a small change in the environmental pH or ionic strength will have a large effect on the distribution and thus, except within a critically narrow range, the solute tends to occupy one phase to the exclusion of the other. The narrow critical range is of course highly dependent on the properties of the solute and this effect can therefore be utilised for separation. This is a fortunate circumstance since the modified celluloses are fibrous in nature and are thus not ideal for packing long chromatographic columns.

In view of the remarkable success of the cellulose-based ion-exchange reagents in analytical work and small-scale preparations it may be anticipated that widespread development in technical applications will not be long delayed. We may expect that for large-scale work the column will be largely replaced by adsorptive filters of no great depth with a succession of eluents rather than a gradient.

This technique is well illustrated by the experiments of Rhodes *et al.* (16) on the fractionation and purification of egg white proteins. In this work, ovomucoid, ovalbumin A<sup>1</sup> and A<sup>2</sup>, conalbumin, avidin, lysozyme and several different unidentified globulins were separated directly from egg white in a substantially pure state by stepwise elution from a column of carboxymethyl cellulose. Larger-scale preparations of individual proteins were carried out batchwise by stirring the exchanger (3-5 g. of CM-cellulose per g. of protein adsorbed) with a solution of the protein in buffer at a pH approximately 0.5 unit more acid than the isoelectric point of the protein. The suspension was then filtered and washed, and the desired protein eluted by stirring with a buffer at a pH more alkaline than the isoelectric point of the protein. In this way crude preparations of 10-20 g. made by conventional salting-out methods could be obtained in a highly purified condition by a single batch process only.

The concentration of dilute solutions of proteins could also be carried out in the same way. Thus in one experiment with conalbumin a 20-fold concentration was obtained by adsorbing the dilute solution in acetate buffer of pH 5.5 on to CM-cellulose and then eluting with phosphate buffer of pH 8.6.

It should finally be noted that batch operations and operations with short columns have the advantage that they can be completed relatively quickly and therefore most separations can be carried out near room temperature with little risk of bacterial spoilage. Some degree of temperature control may still be necessary, however, since it is known that the ionisation of the polar groups on cellulose ion-exchangers is remarkably sensitive to changes in

temperature and this affects the adsorption equilibria (17). The properties of the cellulose reagents make them ideally suited to fluidisation techniques and there seems to be little doubt that very-large-scale purifications could be conducted by their use in batch processes occupying only a few hours and employing standard equipment.

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## **BIOLOGICAL PRODUCTS**





## **FATS AND FATTY OILS**

**By MEMBERS OF THE OILS AND FATS GROUP**

**(Convenor: H. JASPERSON, B.Sc., Ph.D., F.R.I.C.)**

As in last year's Report, there is included a section on some selected aspect of fats not hitherto covered.

In preparing a summary of present knowledge of 'Lipids in Relation to Ruminant Nutrition', it has not been possible to record all the available references to several of the topics discussed, especially those pertaining to earlier studies, the results of which have led to many of the current findings, although these are acknowledged in the appropriate publications which are cited. Detailed discussion of the more biochemical aspects has been purposely avoided in an attempt to give a balanced account for the agricultural chemist and those concerned with the manufacture of feedingstuffs.

### **SUPPLY OF OILSEEDS, OIL MILLING AND SOLVENT EXTRACTION (J. L. R. Pritchard, B.Sc., A.R.I.C.)**

World production of vegetable oils and oilseeds has been reviewed by the Commonwealth Economic Committee (1) and Faure (2), who has included the production of marine oils and animal fats.

Revised estimates of world production (2) for 1958 at 29.3 million tons (metric) and for 1959 at 31.6 million tons show a surprisingly large increase. It must be explained, however, that most of the increase is due to the availability of detailed statistics of domestic production from the U.S.S.R. Final figures for 1960 are expected to show that increase in both production and exports has been maintained and must continue into the foreseeable future to keep pace with demand.

In the U.K. the crush rose by 11% to 1,047,000 tons. The increased oil production was small but production of cake/meal rose by 20%. This reflects increased processing of soya-bean at the expense of copra and palm kernels.

The future pattern of the industry, both in the U.K. and Western Europe, was discussed in detail at the recent Congress of the

International Association of Seedcrushers held in London (3). Concern was expressed at the development of seedcrushing in the seed-producing countries, the inherent trade restrictions, and the possible effect on product quality. Albeit there is a general agreement that expansion of the broiler industry will entail an increased seed throughput of low oil content seeds such as soya-beans, while the total oil output may decline.

### **Oil milling and solvent extraction**

#### *Analytical techniques*

The problem of residual solvent in extracted meals is being more extensively investigated in the U.K. (4) and the U.S. (5).

Gastrock has published some revealing information concerning present techniques, both qualitative and quantitative. Preliminary experiments are reported with a simple concentric-ring, copper cup flash-tester for which repeatable and reliable results are claimed for amounts as low as 0.03% of residual hexane. Interpretation of these results is not such an easy matter. Hexane-extracted meal, for example, in a confined storage space and with total release of solvent will attain the lower explosive limit at 0.006% of residual solvent. Evidence is presented that part of the solvent is bound to the meal in some indefinable manner, dependent on the residual oil. This would raise the critical level. It is suggested that the method may be sufficiently sensitive for plant control.

The relatively new technique of gas chromatography has been applied to the problem of residual petrol in oils (6) and is to be extended to meals. At present the cost and need for a special operator would detract from its general application.

### **Seed pretreatment and expelling**

Processing losses of material (oil- and moisture-free) have been previously correlated with the protein content of the seed and attributed to an intermolecular protein reaction with water elimination. Brawner (7) has summarised evidence on unaccountable oil losses and shows a relation to the free fatty acids (f.f.a.) and oil contents of the seed. Losses in cooking and pressings are insignificant. An overall average loss of 13 lb. of oil/ton of cottonseed is calculated. Castillow (8), however, claims a lower loss of 2.8 lb. of oil/ton of cottonseed with French expellers.

Useful practical information (9) for crushing cottonseed, copra, groundnuts, sesame and soya-beans includes details of seed preparation, cooking and expelling conditions. The trend in expelling (10) towards machines with larger capacity, fundamentally unchanged but with modifications designed to speed up maintenance, continues with the introduction of a new screw press by the French Oil Machinery Co. This press will work up to 300 h.p.

and has an 88-in.-long barrel; performance details will be of interest when available.

Suech (11) has designed a special press for olives and groundnuts which paste up. The seed is rolled to a mass of dough-like consistency and conveyed on chains with serrated links which eventually mesh like gear wheels. Modifications to standard expellers for special purposes such as drying wet polymers (12) and pressing cocoa beans (13) have been described.

### Solvent extraction technique

In a balanced plant the limiting constraint on capacity should be the extraction rate of the material processed. Arnold (14) has pointed out that U.S. industrial hexane may range from 60% to 90% hexane, and he has compared rates of extraction at 140°F of cottonseed and soya-beans over this range of purity. Cottonseed rates were unchanged but soya-beans were extracted more slowly with pure hexane, but pure hexane gave the oils with the best quality.

Upgrading of castor bean meal may result from reported experiments (15) on detoxification and de-allergenisation; meanwhile bench-scale data are now available (16) for direct extraction of the beans by filtration extraction.

Cavanagh (17) claims that addition of soda ash to cottonseed before extraction, followed by addition of soapstock in the desolventiser, renders the meal non-toxic. Clayton (18) uses a similar principle in producing a meal of low free gossypol content, while Fincher (19) uses soapstock or the calcium soap therefrom to facilitate the pelleting of extracted meals.

### Solvent extraction mechanics

Reduction in capital cost and modifications designed to simplify maintenance are the main claims for two new extractors. The French plant is similar in principle to the Rotocel extractor but in this case the baskets are stationary and the feed spout, miscella sprays and meal offtake rotate. Blaw Knox have patented (20) a modified Rotocel plant designed for smaller capacities and space limitations.

Dual evaporation is now being used (10), which entails using desolventiser vapours in the miscella evaporator giving a steam saving of 20% on hexane. Apparently the added investment due to additional evaporator and condenser capacity is only justified for larger plants of about 500 tons/day capacity.

A De Smet desolventiser (21) uses superheated solvent vapour and live steam with the marc making a horizontal traverse of a jacketed vessel on a band conveyor.

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## OIL PROCESSING (A. Crossley, B.Sc., Ph.D., A.R.I.C.)

### Refining and allied processes

FURTHER improvements in methods of continuous neutralisation have been reported during the year and the scope of the process has been extended to include application to the nut oils. Doyle *et al.* (1) have continued their series of publications on the application of the centrifugal 'rotating contactor' to continuous oil neutralisation, with particular reference to palm kernel and soya-bean oils. The continuous neutralisation of crude coconut oil in a pressure system is described by Sullivan (2). In refining oils rich in lauric acid, the mixing time with alkali should be very low and air-entrainment, which leads to the formation of stable emulsions, should be eliminated; these conditions are fulfilled in the 'short-contact' sealed system described. The refining loss during the process has been related to the type of soap phase formed and the refining conditions necessary to obtain the correct phase have been defined to give a 'lauric acid refining zone' in the phase diagram. A practical account is given by Sikes (3) of the various methods which can be used to neutralise cottonseed oil at a mill where the oil is obtained by solvent-extraction. Miscellar refining is compared with several of the more normal continuous-refining methods on a cost basis.

Several improvements in neutralisation technique are described. The concentration and amount of added alkali may be adjusted to obtain a soap stock which has a moisture content not exceeding 1.5 times the soap content (4); the soap stock obtained in this way is granular and can readily be removed in a centrifuge. Improved

yields in soda-ash refining are claimed by removal of carbon dioxide under vacuum (5).

Choudhury & Arnold (6) have developed a simple method for determination of oil loss, suitable for factory application. Pardun & Werber (7) have compared losses determined by laboratory methods with those on the production scale, and emphasise the influence of phosphatide on the laboratory determinations.

A study has been made at the Tropical Products Research Institute (8) of the bleachability of Nigerian palm oil. It was concluded that the main factor influencing the colour of refined oil is oxidation by lipoxidases prior to extraction, although iron-catalysed atmospheric oxidation can further influence the effectiveness of bleaching. The mixing of oils of good and poor bleaching properties may lead to a final oil of poor bleachability. It is suggested that the extent of deterioration of an oil depends also on its carotene content, the oils with a high content giving poorer colours.

Naudet & Drap (9) have discussed the theoretical aspects of decolorisation with bleaching earths and have made a study of the effect of variations in the bleaching process on the colour of groundnut oil (10). A study of oil retention on bleaching earths (11) has shown a fairly consistent inverse relationship between apparent bulk density and oil retention, both in laboratory and plant-scale experiments.

Two new types of deodoriser have been described in patents from the Armour Co. (12) and the de Smet Co. (13). These differ in design but are both constructed to give the maximum contact of oil with steam in a thin film or spray.

### Hydrogenation

A considerable amount of valuable laboratory work has been carried out in the last year on the mechanism of various types of hydrogenation. Hydrogenation in solvent has been investigated for cottonseed oil by Albright *et al.* (14) and for methyl oleate by Cousins & Feuge (15), and has been patented both as a batch process (16) and as a continuous process combined with distillation of the solvent (17). Insufficient data are available for any general conclusions to be drawn, but certain specific facts emerge. For cottonseed oil hydrogenated under realistic factory conditions with a commercial Rufert flake catalyst at 115–145° the presence of solvent has comparatively little effect on selectivity, extent of *trans* isomerism or rate of hydrogenation, although the dependence of rate on hydrogenation temperature, which determines the optimum working temperature, is somewhat affected. On the other hand Cousins & Feuge find that the rate of hydrogenation of methyl oleate with a palladium/charcoal or Raney nickel catalyst at 30° is greatly increased in the presence of solvent; with the nickel

catalyst the solvent reduced the extent of both *trans* and positional isomerism, but with palladium, which strongly promoted isomerism, solvent had no effect.

Zajcew (18) has made a practical investigation of the hydrogenation of various oils with a palladium/charcoal catalyst. This catalyst is extremely active, usually selective, and the *trans* content of the hardened product can be regulated by control of the hydrogenation conditions. He concludes that commercial application is promising and describes the pilot-plant preparation of a shortening with low *trans*-acid content. In pilot-plant experiments 1 g. of 5% palladium on charcoal was used to hydrogenate 18 kg. of soya-bean or cottonseed oil.

Temperature has been shown (19) to be the main factor affecting the isomerisation of the double bond during hydrogenation of methyl oleate. As the temperature increased from 96 to 200°, the proportion of double bonds remaining in the original position fell from 74 to 17% for a hydrogenated product of similar unsaturation. The use of palladium led to even greater double-bond migration but sulphur poisoning of the catalyst had little effect. The proportion of *trans* double bonds increased with increasing migration of the double bond but the effect was not proportional.

The hydrogenation is described (20) of fatty acids in the vapour phase with a fluidised bed catalyst. Unlike liquid-phase or fixed-bed hydrogenation, the reaction proceeds rapidly at reduced pressures and comparatively low temperatures. The process is suitable for continuous operation.

#### **Margarine, shortenings, etc.**

A number of modified fats have been described which contain varying amounts of short-chain acids. These are prepared either by inter-esterification of natural fats with short-chain glycerides or by re-esterification of fatty acids with glycerol. The modified fats have an increased plasticity range and can be used according to composition in margarine, mayonnaise or in salad oils. In typical patents (21), coconut oil or hardened coconut oil is inter-esterified with 5 to 30% of the triglyceride esters of fatty acids with 6, 8 or 10 carbon atoms, and with 5 to 30% of tripalmitin or tristearin. An oil suggested for use as a salad oil or for medicinal purposes is prepared entirely from short-chain components, mainly caprylic acid (21b). Improvements in consistency and in cake-making properties of lard are said to result from random inter-esterification (22a), and the production of a butterfat substitute is claimed by inter-esterification of lard and coconut oil (22b). An inter-esterification process is described by E. F. Drew & Co. (21c) in which coconut oil and higher fatty acids are inter-esterified in a heated reaction vessel; lower fatty acids distil from the column during the reaction.



Free-flowing powders with a high fat content are described. The powders are produced by spray-drying or by extruding into a precipitating solution. In one case a free-flowing, high-protein dietary supplement containing 30–40% of fat is claimed (23), and in a second patent (24) the powder is obtained by spraying an aqueous emulsion containing a polyuronide and contains 95% of hydrogenated groundnut oil.

Many patents have appeared recently on the production of sharp-melting confectioner's fats or cocoa butter substitutes. One type of product is prepared by solvent fractionation of natural fats such as lard, tallow, palm oil or shea butter, usually from acetone (24b). Alternatively the starting material may be hydrogenated before or after the fractionation to give a product of the required melting point with an increased yield (25). A second type of substitute, rich in lauric acid, may be prepared by re-esterifying the required fatty acid mixture rich in lauric acid with glycerol (26) or by hydrogenating nut oils and inter-esterifying the product (27) which may then be fractionated from solvent (28).

An interesting process for producing a butter substitute is described by Duin & Schoop (29). A heat-stable oil-in-water emulsion of an oil is prepared in the presence of an emulsifier. A part of the dispersed phase is allowed to solidify and partial phase inversion is effected by mechanical working. The nature of the emulsifier is very important in this process and one suggested as particularly effective is sodium *N*-stearoylsarcosine.

In a paper by Hoerr (30) the general performance of shortenings, and particularly the effect of incorporation of air, has been correlated with the crystal and polymorphic forms present. On the basis of this information the most satisfactory raw materials and optimum processing conditions for shortening manufacture are discussed.

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#### ANALYTICAL METHODS (N. W. Hanson, B.Sc., Ph.D., F.R.I.C.)

ADVANCES in analytical methods continue to comprise the refinement of existing techniques and the application of new ones, rather than the development of new methods specifically for oils and fats. Signal advances would therefore appear to depend upon the introduction of radically new general techniques such as that of gas-liquid chromatography. The greatly increased resolving power

conferred by applications of recent techniques is enabling analysts to pay more attention to such problems as the adulteration, the development of oxidative breakdown products and the detection and determination of very minor constituents of oils and fats. Increasing attention is also being paid to artefact formation during the course of analysis, and milder methods are being sought in attempts to overcome this.

### Spectroscopic methods

Further studies have proceeded on ultra-violet spectrophotometry after isomerisation of non-conjugated to conjugated unsaturation in fatty acids by means of potassium *t*-butoxide in *t*-butanol (see Reports for 1957, p. 284, and 1958, p. 312). White & Quackenbush (1) found that during isomerisation the absorptivity values at 233 and 268  $m\mu$  reached a maximum, after which they decreased with time. They described a simple procedure for isomerisation with the alkoxide in a reagent bottle at 60° for 20 h., the results being in good agreement with those obtained by KOH in glycol (A.O.C.S. method Cd 7-58). The 1958-59 Report of the A.O.C.S. Spectroscopy Committee (2) states that the tentative method for the direct determination of *trans* acids by infra-red absorption is not satisfactory and recommends further work. Acids can, of course, be successfully analysed by first converting them to their methyl esters, and the Committee recommended a tentative method of infra-red absorption at 10.3  $\mu$  for isolated *trans*-isomers. Cleverley (3) has overcome difficulties arising from spectral interference in the infra-red determination of unconjugated *trans* unsaturation by a compensation method that separates graphically the overlapping bands around 965  $cm^{-1}$ . The influence of molecular structure on the infra-red absorption method for *trans*-isomers has been demonstrated by Kaufmann and others (4), who showed that structural effects in certain glycerides led to appreciable positive errors. The glycerides should therefore be hydrolysed and the fatty acids converted to their methyl esters before infra-red examination. The near-infra-red region (see Reports for 1958, p. 313, and 1959, p. 155) has been used by Fenton & Crisler (5) for determining the *cis* unsaturation (absorption at 2.143  $\mu$ ) in refined and hydrogenated oils and in finished shortenings. The method is applicable to *cis* polyenes as well as *cis* monoenes, and to mixed esters and fatty acids, and allowance can be made for the effect of *trans* fatty acids.

### Chromatography

In the *gas-liquid chromatography* of fatty acid methyl esters it has been usual to refer the relative retention times of the components to a known component. Woodford & van Gent (6) have

presented the elution sequence by plotting the retention times of the saturated straight chain esters against chain length on a semi-logarithmic scale. The value corresponding to the retention time of any other peak then gave the chain length ('carbon number') of the hypothetical saturated straight-chain ester that would be eluted at that point. The carbon numbers for saturated straight-chain esters were integral, whereas those for branched chain and unsaturated esters were non-integral. The carbon number was characteristic of a particular ester on a particular stationary phase.

When investigating mixtures of several components by gas-liquid chromatography it may be necessary to use additional identification methods to the retention value or retention time, and Hallgren *et al.* (7) have applied mass spectrometric methods to fractions collected from the gas chromatography columns. In this way, complex mixtures of fatty acids present in butter and margarine could be analysed. Craig & Murty (8) determined the fatty acid compositions of vegetable oils and of two synthetic mixtures of methyl esters by gas chromatography, and also by calculation from standard methods (iodine values and spectral data), and found that the gas-liquid partition chromatography data were reliable to within one unit per cent. Standard methods gave lower values for linoleic acid and higher values for linolenic acid than did gas-liquid partition chromatography, and this deviation was particularly evident when a high proportion of linolenic acid was present (e.g., in the case of linseed oil).

The thermal stability of the polyesters used as stationary phase could be improved by using the succinates of 1,4-butanediol or ethylene glycol rather than those of diethylene glycol.

Hornstein *et al.* (9) concentrated the naturally occurring free fatty acids in cooked and cured meats by adsorbing them from light petroleum solution on to an anion-exchange resin stirred with the solution. The adsorbed acids were converted to their methyl esters directly on the resin with anhydrous methanolic hydrochloric acid, the methyl esters extracted with light petroleum ether and analysed by gas chromatography on 'Chromosorb' coated with polyvinyl acetate. Quantitative determination was made with n-heptadecanoic acid as added internal standard.

Various methods of preparing the methyl esters of fatty acids before chromatographic separation are in use, and the methanolysis procedure with a large excess of alkali methoxide in absolute methanol has been shown by Luddy *et al.* (10) to give substantially quantitative yields from cholesterol esters, phospholipids and glycerides. These authors used a silicic acid absorption column to separate the methyl esters from unsaponifiable matter and free fatty acids. A departure from the methyl ester technique has been described by Kibrick & Skupp (11), who synthesised 1-bromo-2-chloroacetophenone, and prepared eight fatty acid esters with this

reagent. The melting points and absorptivities of 257  $m\mu$  of these esters were reported and the separation of the eight fatty acid esters by chromatography on a column of polyethylene and 'Celite' and elution with various proportions of alcohol were presented.

A type of adsorbent separation known as *thin-layer chromatography* is being developed as an alternative to paper chromatography for certain types of analysis. Thus, synthetic antioxidants can be satisfactorily chromatographed on a layer of silica gel containing a little gypsum and fixed to a glass plate or strip (12). Again, Mangold & Malins (13) found that thin layers of silicic acid or alumina permit rapid fractionation of complex lipid mixtures according to the classes of compounds, and good separations are obtained with much less material than is required with standard techniques of column chromatography. The spots were usually smaller and more distinct than those obtained in cellulose or glass-fibre paper chromatography.

*Paper chromatography* continues to hold an important place in the analysis of lipid mixtures. Its scope is being amplified by further treatment, e.g. by hydrogenation, acetylation, etc., of the constituents of spots thus separated, and rechromatographing after such treatment. Kaufmann and co-workers are making considerable use of these methods, e.g. in analysis of critical fatty acid mixtures containing palmitoleic, myristic and linoleic acids, which have the same  $R_f$  values (14). The fatty acid mixture was chromatographed on paper with the system undecane-acetic acid-acetonitrile. The spots were made visible by treatment with copper acetate to form the copper soaps; after removal of excess copper acetate and addition of dithio-oxamide (rubeanic acid), the brown spots could be evaluated photometrically or eluted with benzene and re-chromatographed. The spots containing the 'critical' mixture were re-chromatographed, the transferred acids hydrogenated and the resultant saturated acids (palmitic, myristic and stearic) were then separated chromatographically. Animal fats were analysed in this way, and the iodine and thiocyanogen values were calculated from the composition found; the results agreed with those determined on the original mixture.

An interesting chemical method has been employed by McInnes *et al.* (15) for determining monoglycerides in terms of their constituent fatty acids. The monoglyceride mixture was mesylated with mesyl (methanesulphonyl) chloride, and the resulting dimesyl derivatives converted to the allyl esters of the constituent fatty acids by treatment with sodium iodide. Both  $\alpha$ - and  $\beta$ -monoglycerides were quantitatively converted to allyl esters by this procedure. The allyl esters were then submitted to gas/liquid partition chromatography; peak heights of  $C_8$ – $C_{12}$  esters and peak areas of  $C_{14}$ – $C_{18}$  esters were proportional to the weight concentration.  $\beta$ -Monoglycerides in a mixture of  $\alpha$ - and  $\beta$ -isomers

could be determined separately after removal of the  $\alpha$ -isomers by oxidation with periodic acid.

### Unsaturation

A spectrophotometric method for determining oleic, linoleic and linolenic acids in fats and oils, depending on colour reactions of the esters and glycerides with ferric chloride or mercuric acetate, has been described by Rhodes (16). The esters, if soluble, are treated directly with the reagent in the presence of glacial acetic acid and concentrated sulphuric acid or, if of low solubility, are partially transmethyated first. The mercury complexes that are formed with unsaturated fatty acids have been used (17) to augment the differences in solubility, so that countercurrent fractionation of the complexes can be used to separate sufficient of the test substances for structure analysis to be made. Mercury in the fractions is determined by the dithizone method. The less highly unsaturated fatty acids were separated in this way, depending upon the degree of unsaturation and chain length.

### Antioxidants

As limited amounts of *n*-propyl, *n*-octyl and *n*-dodecyl gallates are now permitted as antioxidants in certain foods, it has become desirable to evolve a rapid and reasonably accurate sorting test, and this has been done by Cassidy & Fisher (18). The normal method for determining gallate was unsatisfactory in methanolic solution, but when the gallate solution was shaken with solid ammonium ferrous sulphate a clear and stable blue solution resulted. This solution obeyed Beer's law, and extinction measured at 580  $m\mu$  and multiplied by an appropriate factor gave the amount of gallate present. Berger *et al.* (19) have used reverse-phase partition chromatography to separate butylated hydroxyanisole and gallate esters from fat. The gallate esters were determined colorimetrically after reaction with ferrous tartrate, and butylated hydroxyanisole after reaction with 2,6-dichloroquinone-chloroimide. Wurziger & Chandra (20) have pointed out that the colour reaction with 2,6-dichloroquinone-chloroimide is not specific for butylated hydroxyanisole, but the presence of the latter may be confirmed by means of its pink to red colour reaction with ethanolic potassium hydroxide. Gallates, nordihydroguaiaretic acid and butylated hydroxytoluene also give red colours with ethanolic potassium hydroxide solution, but the colour due to gallates rapidly changes to yellow-brown, that due to nordihydroguaiaretic acid changes to yellow-brown on heating, and that due to butylated hydroxytoluene is ether-soluble.

Methods for determining the stage of oxidation of olefinic fats continue to be developed. Thus, Täufel & Zimmermann (21)

applied hydroperoxide value, benzidine carbonyl value, and thio-barbituric acid malonaldehyde value for the analytical examination of the stage of oxidation reached. A new method for determining organic peroxides has been devised by Treibs (22), who used hydrazine hydrate, which in the presence of catalyst evolves nitrogen by reaction with peroxide, the nitrogen being measured volumetrically. The results were comparable with those by iodometric determination, but were not influenced by the presence of double bonds.

### General

Radioactive reagents are now being used in the analysis of lipids. Mangold (23) converted free fatty acids to methyl esters with  $^{14}\text{C}$ -diazomethane and acetylated hydroxyl and amino groups with radioactive acetylation mixture. Chromatographic methods were used to separate the mixtures, and the components were identified and analysed by radioactive counts and photographic techniques.

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## AUTOXIDATION AND ANTIOXIDANTS (L. A. O'Neill, M.Sc., Ph.D.)

**Autoxidation**

No major advances in the elucidation of the mechanism of autoxidation of unsaturated fatty esters have been reported.

The mixed autoxidation products of fatty esters undoubtedly

contain, in addition to simple hydroperoxides (which will oxidise KI), a variety of other compounds of differing oxidising potential (e.g., compounds which will oxidise HI but not KI). Attempts have been made to follow these potentials polarographically. Kuta & Quackenbush (1) in this way obtained three reduction steps with autoxidised lard.

The elucidation of the nature of the polymeric compounds formed on breakdown of the initially formed hydroperoxides is a particularly complex problem. Frankel *et al.* (2) have examined the dimers formed in the absence of oxygen from methyl linoleate and methyl oleate hydroperoxides at 210° (a temperature encountered in the deodorisation of vegetable oils). The inability of HI or catalytic hydrogenation to split the dimers suggested a C-C linkage between the monomer units, and no evidence was found for a 6-membered ring structure.

Much attention continues to be paid to the nature of the volatile carbonyl compounds formed during the autoxidation of edible oils and fats, which are at least partly responsible for flavour deterioration. Each unsaturated fatty acid may form several isomeric hydroperoxides on autoxidation and these may undergo scission at various points, giving a variety of low molecular carbonyl compounds. Thus, the hydroperoxides of linoleic acid, often the most readily oxidised acid in an edible oil, can give n-hexanal, n-deca-2,4-dienal and 2-octenal as main scission products, and all these compounds have been isolated. Other fatty acids will give other products, and breakdown of secondary oxidation products formed from the hydroperoxides can lead to a variety of compounds. Twenty-one carbonyl compounds found on autoxidation of olefinic fats have been listed by Täufel & Zimmermann (3).

Modern instrumental methods are facilitating the analysis of these complex mixtures containing many trace components. A common procedure is to isolate the mixed carbonyl compounds in the form of a derivative and then to recover and separate the individual components.

A new technique known as 'flash exchange gas-chromatography' has been developed and used by Ralls (4) for the semi-quantitative determination of volatile carbonyl compounds responsible for vegetable flavours, and should be adaptable for the investigation of fat deterioration problems. In this method a derivative of the volatile compound, e.g., the 2,4-dinitrophenylhydrazone, is rapidly heated (250° for 10 sec.) with a suitable reagent, e.g.,  $\alpha$ -ketoglutaric acid, and the products volatilised into the gas chromatography unit and analysed. Methods for the regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones without introducing odours which might interfere with organoleptic examination have been studied and the most suitable procedure found to be treatment with sulphuric acid (5).

Ion-exchange methods have also been used to separate the carbonyl compounds in fats (6).

As indicated, an important degradative autoxidation product of edible oils is *n*-deca-2,4-dienal. Hoffman & Keppler (7) found in the volatile decomposition products of autoxidised palm oil and groundnut oil, two isomeric *n*-deca-2,4-dienals. By gas chromatographic and infra-red analysis of these isomers, in comparison with synthetic products of known stereo-configuration, it was shown that there were the *trans-cis* and *trans-trans*-isomers in the proportion of about 28 : 72.

The carbonyl compounds formed by autoxidation of ammonium linoleate have been examined, the compounds found, viz., *n*-hexanal, 2-octenal and *n*-deca-2,4-dienal, being those given by the ester (8).

Gaddis *et al.* (9) found that preheating of a rancid pork fat at 165° changed both the nature and amount of steam-volatile monocarbonyl compounds. Examination (10) of the distribution of volatile and non-volatile carbonyls in an oxidised lard showed that most of the carbonyl compounds were non-volatile or bound. Girard-T reagent enabled the isolation of 61% of the total carbonyls to be made, but only 4.4% of the carbonyls were free, with 1.4% of volatile monocarbonyls and 1.1% of volatile dicarbonyls.

Malonic dialdehyde is another breakdown product considered to be formed during the autoxidation of fats and responsible for the colour reaction with thiobarbituric acid. Tarladgis (11) has studied the conditions for its determination. A procedure involving distillation of the (meat) fat in presence of water at pH 1.5 and treatment of the distillate with the reagent was found most satisfactory. In controlled oxidation experiments, it was shown that the malonic dialdehyde was not a stable end-product, but that its concentration passed through a maximum (12).

The effect of refining treatments on the stability of oils has been examined: neutralisation and bleaching reduced, but deodorisation increased, the stability of olive oil (13). The flavour and oxidative stability of soya-bean oil have been shown (14) to be related to the degree of autoxidation of the oil prior to deodorisation. The non-volatile carbonyl compounds derived from the hydroperoxides during processing are believed, on the basis of parallel studies on soya-bean oil methyl esters, to contribute to the flavour deterioration.

Increasing attention is being paid to the autoxidation of oils and fats in aqueous emulsion systems, where significant difference in oxidation rates and antioxidant behaviour are observed, as compared with the dry material.

Spetsig (15) in a comprehensive series of eight papers has studied the effect of pH, components present in the emulsion system, and antioxidants and synergists on the autoxidation of methyl lin-

leate. It was found that (i) the various components present in food and cosmetic emulsions could accelerate or retard oxidation, (ii) antioxidants, e.g. polyhydroxyphenols, could be extracted into the aqueous phase and lose their activity, (iii) the antioxidant activity of phenols or amines usually decreased at high pH and protection at pH > 9 was difficult, (iv) butylated hydroxyanisole (BHA) was one of the most active antioxidants in presence of water, (v) the action of synergists was specific for the system and varied appreciably with pH.

Mabrouk & Dugan (16) examined the kinetics of autoxidation of methyl linoleate and linoleic acid in aqueous emulsion. Sodium chloride was found to retard the autoxidation. The rate of autoxidation of the ester increased with pH but that of the acid showed a maximum at pH 5.5.

Bishov *et al.* (17) studied the autoxidation of fats in dried emulsion systems resembling those found in dehydrated foods; certain porphyrin compounds showed pronounced pro-oxidant activity; phospholipids retarded oxidation, but some of the common phenolic antioxidants were relatively ineffective.

The behaviour of oxidation catalysts in emulsion and non-aqueous systems has been compared by Schuler *et al.* (18).

### Antioxidants

The mechanism of action of antioxidants, even of the phenolic type, is not fully understood. Phenolic antioxidants are believed to affect the chain-propagation step, becoming oxidised themselves in the process. Fueno *et al.* (19) have studied the relation between the antioxidant activity of a wide range of phenols and their oxidation potentials predicted from calculated orbital energy data. They suggest that the rate-determining step of the inhibition involves an electron transfer from phenol to radicals.

Antioxidants show some specificity of action and it is necessary to choose an antioxidant which is effective for a particular fat or oil under the conditions to be encountered. Results illustrating this point have been obtained by Lea (20), who compared the activity of a range of antioxidants at 37° and 50° for the methyl esters of cottonseed, linseed and cod liver oil fatty acids, with a trace of pre-oxidised ester as an oxidation starter. Whilst mono-*t*-butyl-quinol (MBQ) was always effective, the activities of the other compounds varied appreciably with the nature of the ester and to a smaller extent with the temperature.

A comparison has been made of the antioxygenic activity (for methyl oleate) of lecithin and its hydrolysis products. The antioxidant activity appeared to lie in the phosphoryl grouping (21).

Following the observation that fatty acids often decrease the effectiveness of antioxidants, it has been found (22) that many oil-

soluble bases can act as synergists. Effects tended to be specific: primary, secondary and tertiary amines greatly increased the protection given to oils by 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (EMQ), but on the other hand had no action with 2,6-di-*n*-butyl-4-methoxyphenol (BHT).

### *Tocopherols*

Investigations on the structure, antioxidant action and analysis of the tocopherols continue. It was indicated in the last Report that  $\epsilon$ -tocopherol and  $\xi$ -tocopherol were found to be not identical with 5-methyl and 5,7-dimethyl tocols respectively, as previously thought, and the structural evidence has now been published by Green *et al.* (23).  $\epsilon$ -Tocopherol is now considered to be 2,5,8-trimethyl-2-(4,8,12-trimethyltrideca-3,7,11-trienyl)chroman-6-ol. Natural  $\xi$ -tocopherol from wheat bran appears to be a trisubstituted derivative in the same series, but that occurring in rice is an authentic 5,7-dimethyl tocol.

The mechanism of action of tocopherol (24), inversion effects (25), and stability to oxidation (26) and storage and heating (27) have been studied.

A report of a collaborative investigation on the determination of tocopherols in oils, food and feeding stuffs has now been published by the Analytical Methods Committee of the Society for Analytical Chemistry (28). The analysis may require up to seven steps involving isolation of the tocopherols, separation into individual tocopherols by two-dimensional paper chromatography and spectrophotometric determination after treatment with a suitable reagent. A specific method for the spectrophotometric determination of  $\alpha$ -tocopherol has been described by Lambertsen (29).

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#### Analysis

(Determination of antioxidants, see section on Analytical Methods)

#### Patents

- Eastman Kodak Co., B.P. 813,538; U.S.P. 2,944,908
- Universal Oil Products Co., U.S.P. 2,903,368; 2,921,850; 2,926,093
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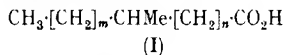
## FATTY ACIDS AND THEIR NATURAL AND SYNTHETIC DERIVATIVES (F. D. Gunstone, Ph.D., A.R.I.C.)

### Fatty acids

THE natural occurrence of a number of hitherto undescribed acids has been reported during the year. Unsaturated  $C_{20}$  ( $\Delta^5$ , 65%) and  $C_{22}$  acids ( $\Delta^3$ , 7%, and an unidentified acid, 10%) are present in *Limnanthes douglasii* seed oil (1). Additional details of dimorphic acid (9-hydroxyoctadeca-*trans*-10, *trans*-12-dienoic) and of two related acids (9-hydroxyoctadeca-*trans*-10, *cis*-12-dienoic and 13-hydroxyoctadeca-*cis*-9, *trans*-11-dienoic acid) are now available (2). The seed oil of *Asclepias syriaca* contains 11-octadecenoic acid (15%) alongside the more familiar oleic and linoleic acids (3) and Kaufmann & Sud (4) have concluded that  $\alpha$ -parinaric acid is either the 9c, 11t, 13c, 15t-, 9t, 11c, 13c, 15t-, or the 9t, 11c, 13t, 15c-octadecatetraenoic acid (t=*trans*, c=*cis*). Additional sources of

epoxy acids are the seed oils of *Clarkia elegans* and *Malope trifida*, and several spores of plant rusts and other fungi (5). The toxic nature of *Dichapetalum toxicarium* seeds, which make them of potential value as a rabbit poison, has been related to the presence of  $\omega$ -fluoro-oleic acid and another fluorine-containing saturated acid (6). In further work on menhaden body oil (see last year's Report), 23 acids, accounting for 95% of the unsaturated acids, have been structurally defined. Six of these are new: the  $\Delta^{7,10,13}$  (0.2%),  $\Delta^{8,9}$  (0.4%),  $\Delta^{9,12}$  (1.6%) and  $\Delta^8$  (1.4%)-C<sub>16</sub> acids, the  $\Delta^{6,9}$ -C<sub>18</sub> acid (0.5%), and the  $\Delta^{6,11,14,17}$ -C<sub>20</sub> acid (0.4%) (7).

The ability to identify even complex mixtures of mono- and dibasic acids by gas-liquid chromatography is the basis of two new methods of structure determination. Murray (8) has shown that a branched-chain acid of structure



when oxidised with permanganate in acetone provides a series of branched chain acids (C<sub>m+n+4</sub>—C<sub>m+4</sub>), a methyl ketone (C<sub>m+3</sub>), and a series of normal acids (C<sub>m+1</sub> downwards) which clearly identify the acid (I). The secondary oxidation of saturated acids, which is an undesirable side-reaction of the oxidative degradation of unsaturated acids, is thus turned to good effect. Oxidation with chromic acid occurs preferentially at the tertiary carbon atom in structures of type (I) so there are fewer oxidative fragments to be identified (9). Certain difficulties in determining the structure of polyethenoid acids are overcome in a new procedure: the acid is only partially oxidised by performic acid and then hydrogenated to a mixture of saturated dihydroxy acids, which are degraded by von Rudloff oxidation to a series of mono- and dibasic acids. The chain lengths of the original acid and the position of each double bond are thus indicated (10).

Papers have appeared on esterification by methanolysis, reaction with diazomethane, and reaction with 2,2-dimethoxypropane (11), the emphasis being on rapid methods for small-scale working. Brandner & Birkmeier (12) concluded that the primary hydroxyl groups of glycerol are esterified more readily than the secondary hydroxyl groups by a factor of 2.3 at 200° and 6–10 at room temperature. The esterification of oleic acid catalysed by certain divalent metal salts has also been studied (13).

Weedon *et al.* (14) studied the fission of (a) monoethylenic acids, (b) diethylenic and acetylenic acids, and (c) keto- and hydroxy-acids, by reaction with molten potassium hydroxide. Mono-olefinic acids give, first a mixture of isomers by reversible migration of the double bond in both directions along the chain, and finally a high yield of the saturated acid having two fewer carbon atoms (Varrentrapp reaction). Linoleic and stearolic acids both give myristic acid

as the major product. Hydroxy-acids are oxidised to keto-acids which are degraded to mono- and dicarboxylic acids by fission at each side of the carbonyl group; the reaction with 12-hydroxystearic acid, 12-ketostearic acid, and ricinoleic acid is reported.

### Glycerides and waxes

Detailed results of component acid analyses are not given but references are given in the Supplementary Bibliography.

Wolf and his colleagues (15), in continuance of their search for new industrial oils, have examined 13 oils of high iodine value, 16 species of *Compositae*, and a further 158 species from 52 plant families. For each oil the iodine value, saponification value, refractive index, hydroxyl value, carbonyl value, epoxide value, percentage of saturated, mono-, di and tri-ethenoid acids, and anything unusual about the infra-red spectrum, are given. Oils of special interest are being examined further.

The final word on the subject of glyceride structure is still unsaid. Kartha's views have been criticised by Lakshminarayana & Rebello (16), who have made a critical study of oxidation methods in the determination of glyceride composition. Some of Kartha's methods of calculation have also been criticised (17). Enzymic hydrolysis continues to attract attention: it has been used by Tattrie (18) to determine the position of saturated and unsaturated fatty acids in egg lecithin, and Vander Wal (19) has discussed calculations based on lipase hydrolysis data. Desnuelle & Savary (20) consider that the structure of natural glycerides is not random, the position of the fatty acids depending on the chain length of the saturated acids and on the degree of unsaturation of the unsaturated acids. In vegetable oils saturated acids occur mainly at the 1- and 3-positions and unsaturated acids at the 2-positions; in animal fats the distribution is less rigid. Enzymic hydrolysis studies of phospholipids have been re-assessed and new conclusions bring these compounds into line with triglycerides: saturated acids predominate at the 1-position and unsaturated acids at the 2-position (21).

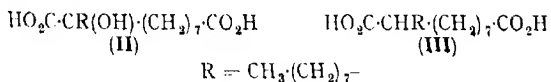
Youngs (22) has proposed a new theory of glyceride structure which is said to give a random or modified restricted random distribution and a predominance of specific positional isomers. Random attachment of fatty acid at each stage of glyceride synthesis is accompanied by intramolecular rearrangement to a preferred form at the 1,2-diglyceride level. The same author emphasises the need for further study of glyceride structure and it is good to be able to report attempts to separate triglycerides by paper chromatography (23) and by gas-liquid chromatography (24), and a procedure for the determination of fully saturated glyceride involving reaction of unsaturated glycerides with mercaptoacetic acid (25).

An investigation of sugar-cane wax has shown the presence of long-chain aldehydes, possibly present in polymeric form, along with hydrocarbons, alcohols and acids. There is no conclusive evidence for the presence of esters and some of the products obtained under normal saponification conditions arise from the aldehydes by the Cannizzaro reactions or by aldol condensation and subsequent dehydration (26).

### Derivatives of fats and fatty acids

The increasing use of fats for the production of other chemicals has put a premium on pure acids, which are often more satisfactory for this purpose than the crude natural mixtures; methods of isolating such acids more conveniently and more effectively are thus under continuous review. Oleic (27, 28), petroselinic (29, 30), linoleic (28, 31), linolenic (28, 31, 32), arachidonic (31), erucic (30), ricinoleic (33), and mono-olefinic acids (34) have been isolated by various methods including urea adduct formation (27, 30), crystallisation (27, 29, 34), adsorption chromatography (28), and counter-current distribution (31, 33). The conversion of erucic acid to the cyclic compounds exaltone and exaltolide, and of kamlolenic (18-hydroxyelaeostearic) acid to exaltone and dihydrocivetone are typical of attempts to convert fatty acids into more valuable compounds (35).

There is continued study of the properties of dibasic acids and their derivatives and of their preparation from fatty compounds by oxidation of unsaturated acids with ozone (36) or with oxygen in the presence of a cobalt salt as catalyst (37). The substituted sebacic acid (II) is formed in good yield (60-70%) when threo- or erythro-9,10-dihydroxystearic acid is fused with alkali; the 9,10-diketo-acid gives a lower yield of the same product. Esters of (II) are too heat-sensitive to act as lubricants and the octyl side-chain renders them less effective as plasticisers than esters of sebacic acid. The 2-ethylhexyl ester of (III), derived from (II), shows promising lubricant properties (38).



Current interest in castor oil and ricinoleic acid is reflected in the number of publications concerned with these substances. The topics covered include the isolation of ricinoleic acid (33), the preparation and properties of ricinoleoylmorpholine and related compounds (39), urethane coatings based on castor oil (40), and the pyrolysis (41), oxidation (42) and alkali-fission of ricinoleic acid (43).

Glycerides in which one or more long-chain acyl groups have

been replaced by acetic acid (44) or by dibasic acids such as succinic and adipic (45) continue to attract attention. Glycerides of dibasic acids provide a series of compounds ranging from hard high-melting waxes to non-crystallising viscous oils and it has been suggested that they might be used as coating materials in the food industry. Esters of carbohydrates have also been examined as potential surface-active agents: their polyoxyethylene derivatives have increased water solubility (46).

Vinyl ethers of linseed and soya-bean alcohols and vinyl esters of keto-stearic acid have been prepared and examined (47). Elaeostearic acid or tung oil reacts as a diene with various dienophiles (methyl vinyl ketone, divinyl sulphone, dimethyl maleate, methyl acrylate, and acrylonitrile) and the products, which have some interest as plasticisers, may be further modified by subsequent hydrogenation or epoxidation (48).

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## LIPIDS IN THE NUTRITION OF RUMINANTS

(G. A. Garton, Ph.D., D.Sc.)

### Feed lipids

RUMINANTS, both wild and domesticated, consume large quantities of herbage (largely grasses and other leaves) the lipid content of which is quite low although, on a dry matter basis, it usually amounts to 5–10%. The lipids consist of glycerides together with smaller amounts of phospholipids, free fatty acids, sterols, waxes and hydrocarbons; fatty acids (free and combined) make up about 50% of the total lipids. The fatty acid composition of the acetone-soluble lipids (i.e., most of the total lipids) of pasture grasses was determined by Shorland (1) and Jasperson & Burke (2) who showed that 75–80% of the total acids consisted of  $C_{18}$  unsaturated components, mainly linoleic and linolenic acids. The acetone-insoluble lipids (phospholipids) of cocksfoot grass were found by Smith & Chibnall (3) to be mainly lecithins and cephalins of which the major component fatty acids were linoleic, linolenic, palmitic and stearic acids. In a more recent study (4) the fatty acids of the total lipids of mixed British pasture grasses were found to represent 2.29% of the dry weight and to contain 61.3% of linolenic acid, 13.2% of linoleic acid and 15.9% of palmitic acid, the remainder being made up of small amounts of myristic, palmitoleic, stearic, oleic, arachidic and behenic acids. Only a very small proportion (3.3%) of the total fatty acids was present in triglyceride combination and free fatty acids accounted for 13.5% of the total; most of the total acids were derived from galactosyl glycerides, which were previously shown (5) to comprise about 60% of the acetone-soluble lipids of grasses and clover and which Benson *et al.* (6) isolated from chloroplast lipids.

Domesticated ruminants also consume the lipids of such feeds as hay, artificially-dried grass, silage and concentrates of both cereal and animal origin. The lipids of hay and dried grass will resemble those of fresh pasture, but it is possible that some changes may take place in the component unsaturated fatty acids during storage; in silages made from grass and legumes Ward & Allen (7) found that, on a dry matter basis, no loss of the linoleic and

linolenic acids present in the fresh material occurred. The lipid content of concentrates depends on their origin and, in some materials, on the extent to which processing (e.g., pressing, solvent-extraction) has removed lipid; many of the commonly used vegetable concentrates (e.g., maize meal, linseed meal, groundnut meal, oats, barley, wheat bran) contain glycerides rich in  $C_{18}$  unsaturated fatty acids. Details of the ether-extractable lipid content of concentrates and other feedingstuffs are given by Evans (8).

Although the proportion of lipid in most feeds is quite low, the amount of feed consumed is considerable, leading to the intake of about 500 g. of lipids per day by a cow at pasture and, under conditions of stall-feeding, pregnant and lactating cows may be given rations which provide up to 1 kg. of lipids daily.

### Digestion and absorption

Due to the presence of the capacious rumen the process of digestion and absorption in the adult ruminant is continuous and post-prandial lipaemia cannot be demonstrated (9, 10). After iodinated triglyceride had been fed to cows, the concentration of iodinated lipid in the blood reached a maximum in from 1.5–2.0 days and thereafter declined slowly to a very low value within 5 days (11).

Ingested feed is subjected to degradation and fermentation by the micro-organisms (bacteria and protozoa) which are present in vast numbers in the rumen. Carbohydrates yield, *inter alia*, volatile fatty acids (largely acetic, butyric and propionic acids); proteins can be hydrolysed, amino-acids deaminated, lipids hydrolysed and unsaturated fatty acids hydrogenated. Although the fate of lipids in the rumen has recently been described in detail (12, 13), it is pertinent to summarise some of the main findings here.

When linseed oil was incubated with sheep rumen contents Reiser (14) found a decreased content of linolenic acid and an increased content of linoleic acid which was ascribed to bacterial hydrogenation. Reiser and his associates (15, 16) subsequently examined the depot fats and rumen lipids of steers and goats which had been fed on diets containing glycerides rich in  $C_{18}$  unsaturated fatty acids (cottonseed oil, linseed oil). When compared with those from control animals not given the oils, the depot fats contained more stearic acid and less oleic acid and it was concluded that this was due to the absorption and deposition of stearic acid produced in the rumen by the bacterial hydrogenation of the dietary  $C_{18}$  unsaturated acids; comparison of the iodine value of the total fatty acids of the rumen contents with that of the fatty acids of the oils as fed showed that extensive hydrogenation took place in the

rumen. Other studies on sheep (17, 18), in which the degree of unsaturation of feed lipids was compared with that of rumen lipids, confirmed these observations. Shorland *et al.* (19) incubated oleic, linoleic and linolenic acids singly with sheep rumen contents and found that about 20% of each acid was converted to stearic acid and that *trans* isomers and positional isomers of the unsaturated acids were formed to a considerable extent, especially from linolenic acid.

In all the foregoing studies the entire lipids of rumen contents were saponified before determination of the unsaturation of their component acids. To examine more fully the effect of the micro-organisms on esterified fatty acids, Garton *et al.* (18) incubated linseed oil with sheep rumen contents and extracted the lipids without prior saponification. This resulted in the finding that lipolysis can take place, often leading to the liberation of almost all the esterified fatty acids of the oil. Phospholipids, also, were found to undergo hydrolysis when incubated with sheep rumen contents (20). Further studies (21, 22) with rumen contents taken from fistulated sheep and on the alimentary tract contents of slaughtered sheep showed that microbial lipolysis results in the pre-digestion of much of the feed lipids before the ingesta reach the small intestine—the site of lipid digestion in simple-stomached animals. It was found that hydrogenation can take place while unsaturated fatty acids are still present as glycerides, although apparently more readily after their hydrolysis. Glycerol liberated during the hydrolysis is fermented, giving rise, *inter alia*, to volatile fatty acids, largely propionic acid (see also reference 23). The micro-organisms responsible for hydrogenating double bonds have not been studied in detail, but Wright (24, 25) has shown that, in addition to bacteria, ciliate protozoa are probably involved. Bacteria which hydrolyse glycerides and ferment glycerol have recently been isolated from sheep rumen contents (26).

Numerous reports refer to the digestibility of lipids in ruminants based on a comparison of the amount of ether-extractable matter in feed and faeces. This, at best, gives only an indication of the extent of absorption, since ether does not necessarily extract lipids quantitatively, non-lipids may be extracted and faecal lipids probably include components derived from bacteria of the alimentary tract. However, a few recent examples may be cited; a value of 65.6% was reported (27) for the digestibility of grass lipids in cows and two-months-old calves, whilst for slightly older calves other workers (28) found a value of 45.6%. For cows fed on hay and concentrates, Balch *et al.* (29) reported that 83% of the lipids were digestible. Triglycerides added to feeds are apparently well digested; thus tallow incorporated as 10% of 'starter' rations for calves and lambs was 80% and 87% digestible respectively (30) and more than 90% of the cottonseed oil, hydrogenated cottonseed

oil or castor oil included as 6% of the feed of sheep was absorbed (31). In young calves Brisson *et al.* (32) found that milk fat was almost completely digestible and about 90% of lard in 'synthetic milk' could be digested.

Apart from events in the rumen, very little is yet known regarding the fate of lipids in other parts of the ruminant alimentary tract. No lipolytic activity was found in the saliva of adult sheep (18, 22) and, in the cow, lipase was not detected in abomasal (gastric) secretion (33) or in extracts of upper jejunum (34), although lipase is present in pancreatic juice (34-36). In the suckling ruminant, before the development of an active rumen, a lipase is present in the saliva (37, 38) and this probably assists in the digestion of milk fat.

#### Effect of feed lipids on the digestibility of other feed components

Swift *et al.* (39) found that the digestibility for sheep of all constituents of a mixed feed was increased when maize oil was added to give a total of 6.4% ether-extractable matter in the feed, but that when the amount of supplementary maize oil was increased to give 9.7% of ether-extractable matter the digestibility of all feed components was less than with the basal feed, without added maize oil. An attempt (40) to determine the optimum level of total lipid in sheep diets was not successful; maize oil (3-8%) was substituted isocalorically for starch but the presence of the resulting two variables precluded an unequivocal interpretation of the results. Brooks *et al.* (41) gave sheep a diet containing 32 g. or 64 g. of maize oil or lard daily and observed a very marked depression of cellulose and protein digestion; the effect was counteracted by the addition of lucerne ash to the diet (41-44). The active constituent of the ash was found to be calcium (45); other elements, such as P, Mn, Mo, Co, Zn, Fe and B, were not effective.

More recently Davison & Woods (46) carried out *in vitro* and *in vivo* experiments to study the effect of a range of individual fatty acids ( $C_2$ - $C_{18}$ ) and glycerol on the digestion of cellulose by sheep rumen bacteria. Whereas butyric acid, valeric acid and glycerol significantly increased cellulose digestion *in vitro*, the presence of any  $C_6$ - $C_{18}$  saturated acid or unsaturated  $C_{18}$  acid (oleic and linoleic acids) led to decreased digestion; acetic and caproic acids had no effect. When sheep were given diets containing 5% of maize oil, stearic acid, oleic acid or mixed fatty acids or one containing 1% of lauric acid the digestibility of dry matter, organic matter and cellulose decreased, whilst that of ether-extractable matter increased; all diets, except that containing lauric acid, led to decreased digestibility of mineral matter (ash).

It is known that free long-chain saturated fatty acids inhibit

bacterial growth (47, 48) and thus the effect in the rumen of fatty acids either fed as such or resulting from the bacterial hydrolysis of esterified fatty acids is probably related to their antimetabolic effect on cellulolytic bacteria. It seems likely that the mitigating effect of calcium is due to the formation of calcium soaps. Tillman & Brethour (49) reported that maize oil fed to wether lambs reduced the apparent and true digestibility of calcium and resulted in a decreased calcium retention.

### Feed lipids in relation to tissue lipids and milk lipids

It is well known that the depot lipids (or 'depot fats', as they are more often called) of ruminants are very little affected by diet (as opposed to those of non-ruminants) even when large amounts of such triglycerides as maize oil, linseed oil, soya-bean oil or fish oils are administered (15, 16, 50-52). The fatty acid composition of the depot fats of ruminants and of non-ruminant herbivores has recently been discussed by Dahl (52) and Garton (53). The outstanding characteristics of ruminant internal depot fats are their relatively high content of stearic acid and the absence or almost complete absence of polyethenoid components (linoleic and linolenic acids) which are found to a greater or lesser extent in the fats of non-ruminants which eat the same or similar food. The 'stearic-rich' depot fats of ruminants probably result from the absorption and deposition of stearic acid produced in the rumen by the hydrogenation of  $C_{18}$  unsaturated fatty acids, although the possibility that hydrogenation *in situ* of pre-formed oleo-glycerides also takes place (54) is not excluded. It is of interest to note that before the development of an active rumen the young calf can incorporate dietary polyethenoid fatty acids into its fat depots (55) and that the perinephric glycerides of newly-born calves contain less than 10% of stearic acid (52).

The effects of microbial hydrogenation of dietary unsaturated fatty acids in the rumen lead to the presence of appreciable amounts of positional and geometrical isomers appearing in depot fat (56-58) and butterfat (59, 60-62). In addition, ruminant depot fats and milk fat contain small amounts of higher fatty acids with an odd number of carbon atoms and acids with branched-chains. The former are almost certainly derived from the condensation of propionate (derived from rumen fermentation) with acetate units and the branched-chain acids from a similar condensation with acetate units of isobutyric, isovaleric and 2-methylbutyric acids produced in the rumen by the bacterial deamination and decarboxylation of certain amino-acids (62, 63). Although the triglycerides of the blood plasma of cows resemble depot fat in fatty acid composition, the plasma cholesterol esters are rich in  $C_{18}$  polyunsaturated fatty acids (64), showing that some of these acids

escape hydrogenation in the rumen to become esterified with cholesterol during, or after, their intestinal absorption; further, *cis-cis* ('seed fat') linoleic acid has been identified in butterfat (65).

It has been established within the last decade that the fatty acids of milk glycerides have a dual origin; saturated acids  $C_4$ - $C_{16}$  can be synthesised *de novo* in the gland from acetate, while the remaining acids (largely oleic and stearic) are apparently derived from blood plasma lipids [for recent reviews of this topic see Glascock (66) and Garton (53)]. Before this was known, the influence of dietary fat--and hence blood lipids--on the fatty acid composition of milk glycerides had been studied (67). Specific fatty acids in dietary triglycerides had some effect, e.g., coconut oil or palm kernel oil led to increased amounts of lauric and myristic acids in cow milk fat, rape oil gave rise to small quantities of erucic glycerides and feeding cod liver oil led to increased amounts of highly unsaturated  $C_{20}$ - $C_{22}$  acids and decreased amounts of steam-volatile acids; results similar to those with cod liver oil were also obtained using whale oil (68). On the other hand, the daily feeding to cows of about 100 g. of groundnut, rape, soya-bean and linseed oils (rich in  $C_{18}$  polyethenoid acids) did not lead to the appearance of enhanced amounts of these acids in milk fat (67), probably because of their hydrogenation in the rumen. In connexion with work on bloat control (*vide infra*), McDowall *et al.* (69) gave cows a twice-daily drench of 300 ml. of linseed oil, soya-bean oil or groundnut oil or 125 g. of emulsified tallow for 3 days; this treatment did not affect milk yield or the percentage fat and solids-not-fat content of the milk. Whereas the administration of tallow has very little effect on butterfat composition, the feeding of the large amounts of oils was accompanied by increases of up to 10 units in the iodine value of the butterfat.

The question of whether or not the amount of dietary fat can affect output of milk glycerides has been the subject of many investigations and controversial claims (70). For example, in many experiments at Cornell (71), it was consistently found that increasing the lipid content of grain mixtures fed to dairy cows increased the production of 'fat-corrected' milk. Other workers (72, 73) did not observe a similar effect or did not observe it consistently (74). As a result of further experiments designed to resolve the apparent differences Loosli *et al.* (75) concluded that the non-lipid part of the ration could also affect milk fat output. More recently, Balch *et al.* (76, 77) have shown that not only does the amount and state of division of the roughage significantly affect production of milk fat, but the type of starch in concentrates included in a diet low in fibre affects it too; diets with little hay and much flaked maize depressed milk fat output, an effect not observed when dredge corn was the source of starch (cf. reference 78). Under feeding conditions which result in a

lowered output of milk fat, Rook (79) concluded that a diminished supply of acetate from the rumen to the mammary gland limited synthesis in the gland of the higher fatty acids which are normal components of milk fat glycerides. It is relevant to note that Smith & Dastur (80) found that fasting caused a reduction of 24.2% in the molar proportion of  $C_4$ - $C_{14}$  fatty acids in cow milk fat, while the  $C_{18}$  fatty acids (mostly oleic and stearic) increased by 24.7%.

It thus appears that the possible effect of any given diet on milk fat production must be considered in terms of all its components, but it seems that a certain minimum amount of dietary lipids is desirable. In one of the most recent investigations Dijkstra *et al.* (81) concluded that, for the dairy cow, a daily amount of 300-400 g. of 'crude lipids' from roughage and concentrates together is adequate for normal milk production. Nevertheless, there is scope for much further research on the possible relationships between dietary fatty acids, depot glycerides and milk glyceride formation.

### Lipids and physiological disorders

Lipids appear to be a dietary necessity for the young ruminant. Cunningham & Loosli (82) found that when 2-days-old lambs and kids were fed on a fat-free synthetic milk they became dull and listless and muscular inco-ordination developed before death supervened within a few weeks; control lambs given the same milk with the addition of 2% of lard survived successfully, as did kids which received the milk including 0.25% of lard or 0.36% of linoleic acid. When new-born calves were fed on a fat-free semi-synthetic milk, Lambert *et al.* (83) observed a marked retardation of growth after 3 weeks, whilst after 8 weeks the animals developed diarrhoea and scaly dandruff and hair was lost from the back, shoulders and tail. These signs of lipid deficiency were prevented or recovery was promoted by the addition of small amounts of butter oil, hydrogenated soya-bean oil plus lecithin, or a mixture of fatty acid methyl esters which included linoleate. Linoleic acid is apparently a specific dietary requirement for the very young ruminant. No absolute need for dietary lipids has, as far as is known, been proved for any adult herbivore, although it should be mentioned that they act as a vehicle for fat-soluble vitamins and pro-vitamins, the importance of which in calf nutrition has been emphasised (84).

It is generally agreed that excessive frothing of rumen contents which interferes with the normal elimination of gas is the cause of bloat (85) and that anti-foaming agents are effective in preventing this condition. Reid & Johns (86) successfully treated bloat in cattle fed on clover pasture in New Zealand by the administration of a wide variety of lipids which included arachis oil, linseed oil,

soya-bean oil, olive oil, whale oil, emulsified tallow, cream and lanolin; liquid paraffin, paraffin wax emulsion and vegetable turpentine were also effective, as also were certain detergents and other synthetic surface-active substances (85). The spraying of pasture with arachis oil or tallow, such that a cow ingests 90–180 g. of the triglyceride daily, is a simple means of preventing bloat and it has been satisfactorily employed in both Australia and New Zealand. In the U.S.A. attention has been directed to dispersing suitable oils in the animals' drinking water and encouraging results in cattle and lambs were obtained with a commercial lard 'derivative' (87) and with soya-bean oil (88). Whether the degree of lipolysis of glycerides and the extent of hydrogenation of unsaturated fatty acids are related to the anti-foaming properties of some of the effective substances remains to be investigated.

Muscular dystrophy in cattle, sheep and goats can be due to a variety of causes, amongst which is a dietary deficiency of vitamin E (89). The condition can be exacerbated by the inclusion in the diet of relatively small amounts of polyethenoid fatty acids such as are provided by cod liver oil (90) and linseed oil (91). It is noteworthy that Blaxter *et al.* (90) produced muscular dystrophy in calves which were given 28 g. of cod liver oil daily as a vitamin (A and D) supplement to a dried skim milk ration in accordance with the recommendations of the Ministry of Agriculture & Fisheries in the 1938 edition of the bulletin 'Calf Rearing'. This recommendation was repeated in the 1953 edition, but attention is drawn in the current (1960) edition and also by Evans (8) to the risk which attends the use of cod liver oil in calf rations. The use of stabilised vitamin preparations is considered preferable and, if the addition of fat to dried skim milk is desirable, margarine or lard is recommended.

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## RUBBER AND ELASTOMERS

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### Latex

A MEASURE of the extent of bacteria-induced decomposition in natural rubber latex may be obtained from its volatile fatty acid (VFA) content. The stability of latex is related to the VFA content and it is now shown (1) that VFA formation in ammoniated latex is probably due primarily to the presence of a glucose-amino-acid complex. The addition of ammonia as a stabilising agent leads to an enhanced VFA content and a plantation and laboratory investigation (2) discusses the practical factors which determine the best stage for addition of the ammonia. Factors affecting the stability against coagulation on storage of cold styrene-butadiene (SBR) latex have been investigated (3), and it is suggested that coagulation results from particle dehydration causing (reversible) creaming and (irreversible) aggregation.

The stability of natural rubber latex is greatly reduced when compounded with zinc oxide; a standard method has been developed (4) for determining the mechanical stability of latex, based on the addition of zinc oxide and potassium oleate to the buffered (pH 9.75) system. The method may, with modification, be used for synthetic rubber latex.

The production of rubber foam relies upon gelation occurring before foam collapse. Factors affecting pre-gelation foam stability have been investigated (5) and it has been shown that the rheological properties of the thin film surrounding each foam bubble are important. Elastic or viscous films are able to counteract stress disturbances and reduce strain, thereby inhibiting film rupture.

### Natural rubber and polyisoprenes

#### *Isomerised rubber*

A new series of modified rubbers with improved low-temperature behaviour, based on isomerised natural rubber, has been developed as a result of an earlier observation (6) that natural rubber reacts with thiol acids to give products whose crystallisation rates are markedly reduced. This effect was originally ascribed to the chemical incorporation of bulky thiol acid groups at random along the polymer chain, but it has since been shown to result from *cis-trans* isomerisation about the double-bonds (7), so that the final product is a random copolymer of *cis*- and *trans*-isoprene units. The reaction is effected at high temperatures in bulk, solution or latex form, by agents such as dibenzoyl disulphide,

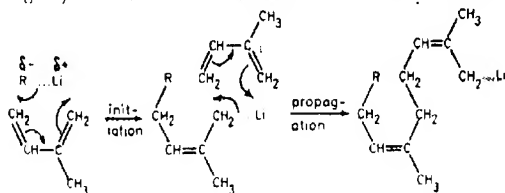
biscyclohexylazocarbonitrile, butadiene sulphone, sulphur dioxide, selenium (8), titanium tetrachloride or aluminium triethyl (9), as well as by thiol acids.

Although the reaction eventually leads to a product containing 43% *cis* and 57% *trans* structures at equilibrium, optimum physical properties are claimed for products containing only 6% *trans* structures, which crystallise about 500 times more slowly than unmodified natural rubber at  $-26^\circ$  (10). The success of small-scale experiments (11) has warranted the production of such crystallisation-inhibited rubbers on the industrial scale (12), and a product has been reported which crystallises almost 1000 times more slowly than natural rubber at  $-26^\circ$ . It was produced by milling (140–190°) natural rubber with butadiene sulphone activated by 1,1'-azo-bis(cyclohexanone-1-cyanide).

#### Synthetic *cis*-1,4-polyisoprene

Although the patent literature abounds with descriptions of stereospecific catalytic systems designed to produce *cis*-1,4-polyisoprene, no systematic description of the process actually used for the production of this polymer on a pilot scale has been available until recently (13). A plant is to be designed to manufacture 25,000–30,000 tons per annum. The pilot-scale plant utilises a Ziegler catalyst system based on aluminium tri-isobutyl (co-catalyst not stated). Pure, dry isoprene is allowed to polymerise at  $50^\circ$  in hexane until the system contains about 25% of solids. The catalyst is then deactivated, antioxidant is added and the solvent removed. Particular care must be taken to ensure that the system is free from traces of oxygen and moisture.

Suggested mechanisms for the Ziegler type of catalyst are largely conjectural (14), but more fundamental investigations have been made of lithium or lithium alkyl catalytic systems (15). These are in current use for producing *cis* polymer, and have the theoretical advantage of homogeneity, unlike Ziegler systems, so that reliable information is more easily obtained. It is now agreed that the *cis*-1,4 polymerisation of isoprene involves a series of polar processes initiated by the reaction of lithium alkyl (LiR) with isoprene to form a lithium isoprenyl alkane ion-pair which, being itself a lithium alkyl, continues to react with isoprene in identical fashion (see Figure). This mechanism differs fundamentally from that of



the non-stereospecific cationic polymerisation initiated by Friedel-Crafts initiators in several respects. The process is a polar (but not ionic) one in which the growing organic chain possesses a fractional negative charge ( $R^{\delta-} \dots Li^{\delta+}$ ), and has been termed anionic. The counter-ion ( $\dots Li^{\delta+}$ ) is an integral part of a six-membered ring reaction transition state. It cannot be allowed to ionise completely and separate from the organic anion if stereospecificity is to be maintained, and this is ensured by the use of strictly non-polar solvents such as paraffins. The presence of polar solvents (e.g., tetrahydrofuran) may be sufficient to form a co-ordination complex with the lithium counter-ion and thus liberate it from the transition state. This is known to give rise to non-specificity. The micro-structure of the polymer is determined by the propagation stage, which consists of a succession of polar reactions proceeding at a rate of the same order of magnitude as the initiation stage. This is very different from non-specific cationic polymerisation, where a slow initiation stage is followed by a series of very rapid ionic reactions.

#### *Vulcanisation of natural rubber*

It has become abundantly clear that a satisfactory answer to the question of what occurs during the vulcanisation of rubber will only be achieved by a combination of both physical and organic chemical methods. These two distinct approaches began to be reconciled some years ago by Flory (16) and more recently by Moore & Watson (17). The latter presented, in effect, a calibration which can be used to obtain a measure of the number of chemical cross-links, present in a sample of vulcanised rubber, from information derived from the equilibrium swelling properties of the rubber sample. This calibration is now beginning to be widely used but it will require modification, since recent work (18) has shown that a certain amount of net-work degradation occurs during peroxide vulcanisation, and this was not allowed for in the original calibration. Attention is drawn to the great difficulty of achieving true equilibrium conditions when making stress measurements on elongated samples of rubber (19), and caution must still be applied in drawing conclusions of a chemical nature from such physical results.

The organic chemistry of the reaction of sulphur with olefins has been re-investigated (20) and the reaction product has been shown to be a mixture of complex sulphides. The product from 2,6-dimethylocta-2,6-diene, used as a model for natural rubber, consists of a monomolecular cyclic monosulphide fraction together with a bimolecular, partly cyclic, polysulphide fraction in proportions which depend on the extent of reaction. The isolation and identification of these products constitutes a major advance in sulphur-olefin chemistry and has provided the basis for a kinetic

investigation (21) of the reaction. This has satisfactorily established that the reaction proceeds by an autocatalytic, polar-chain mechanism and not, as previously supposed, by a radical mechanism. These important conclusions refer only to the non-accelerated reaction of sulphur with model olefins, and application to the accelerated-sulphur vulcanisation of rubber needs caution.

Before mechanistic conclusions can be drawn, it is necessary to know the chemical structure of the sulphurised rubber net-work. The complete insolubility of vulcanised rubber makes it a notoriously difficult material to investigate chemically, but modern organic chemical techniques combined with rubber elasticity theory are now beginning to yield fairly reliable results. For example, it has now been shown (22) that diphenylguanidine (DPG)- and mercaptobenzthiazole (MBT)-accelerated gum-stocks possess cross-links that are predominantly ( $\sim 90\%$ ) polysulphidic, each cross-link containing about 5 sulphur atoms on average, but allowances must be made for net-work entanglements (17). In a non-accelerated vulcanisate, it can be estimated that about 30 atoms of sulphur need to combine with the rubber to yield an effective cross-link, much of the sulphur being combined in elastically ineffective ways involving intramolecular cyclic structures. It is clear that the presence of the accelerator has resulted in a more efficient utilisation of the sulphur in the rubber net-work.

Studies illustrating the complexity of 'sulphurless' vulcanisation of rubber with tetraethylthiuram disulphide (TETD) have shown that during cure the modulus increases at the same rate as the formation of zinc diethyldithiocarbamate, although more slowly than TETD is consumed (23). Finely divided silica 'catalyses' the reaction without changing the Arrhenius activation energy (24). Although reversion is not apparent during thiuram vulcanisation at  $140^\circ$ , it is most evident at  $197^\circ$  (25). Thiuram vulcanisation may proceed by a free-radical process (26), the cross-links being predominantly C-C and C-S-C in nature, with negligible polysulphide groups (27). Degradation experiments elegantly demonstrate (28), however, that thiuram vulcanisates possess mainly polysulphidic cross-links and that 3 atoms of sulphur are combined somewhere in the net-work for every cross-link that is formed. This must not be taken to imply that the cross-links are  $R-S_3-R$  because a certain amount of this combined sulphur is in the form of thiuram fragments attached monofunctionally to the net-work. A review (29) suggests that the cross-links are disulphidic and are inserted by a radical chain process, but a more recent conclusion is that they are polysulphidic and are formed by a polar process (30). The problem is by no means settled.

Use has been made of radioactive sulphur in problems connected with vulcanisation (31). An important conclusion is that MBT

undergoes facile exchange with elemental sulphur and with organic polysulphidic sulphur.

The possibility of a continuous proofing process is suggested by a report that sulphur monochloride vulcanises rubber in a few tenths of a second in the presence of appropriate accelerators (32).

### Oxidation and ageing

Copper and manganese in a rubber-soluble form promote the autoxidation of raw natural rubber and zinc dimethyldithiocarbamate (ZDC) and tetramethylthiuram disulphide (TMTD) are effective protective agents against soluble copper and iron (33). Styrene-butadiene rubber (SBR), unlike natural rubber, hardens on autoxidation, but tris(nonylated phenyl) phosphite is a good all-round stabiliser for raw SBR (34).

'Sulphurless' thiuram vulcanisates were thought to age well because they contain C-C cross-links. It has now been reported, however, that these good ageing properties are due to the accumulation of antioxidants formed as by-products during cure (35). The good ageing properties of TMTD stocks are probably due to the presence of ZDC in the vulcanisate. A recent report shows that these properties may be further improved by incorporating small amounts of copper dimethyldithiocarbamate or even copper oxide into the stock (36). Unlike thiuram-cured systems, radiation-cured systems appear to produce oxidation catalysts during cure (35). Further, the  $\gamma$ -radiation cure of a black-loaded natural rubber stock can be strongly inhibited by the inclusion of 'antirads' (37). These antirads reduce radiation damage, one of the most effective being *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine (38).

The question of whether oxidative degradation of rubber networks results from chain-scission at random along the rubber chain or whether the scission is located at (or near) the cross-links remains unsolved. Recent work on the oxidation of natural rubber gum-stocks (39) and carbon black stocks (40) provides strong evidence in favour of the random chain scission theory. Laevulinic aldehyde was one of the volatile products of oxidation and its yield (per g. of oxygen consumed) was unaffected by the presence of the type of cross-linkages present. On average, 20 molecules of oxygen are consumed for every chain scission. This value is very similar to that previously reported for raw rubber.

A previous report that thin films of natural rubber are rapidly autoxidised in contact with water at ambient temperatures has now been disproved (41).

The mechanism of antioxidant action of amines is still largely unknown, but recent reports suggest that secondary amines function, like phenols, by abstraction of hydrogen atoms (42).

Continuous stress relaxation remains one of the most effective techniques for investigating net-work degradation. It has been stated that stress relaxation rates are very dependent on the chemical constitution of the polymer chain but qualitatively independent of the type of vulcanising system, and that for this reason, stress relaxation is probably due to scission of random chains and not of cross-links (43). These results were obtained with unextracted vulcanisates, however, and they become less convincing in view of reports that antioxidants are produced during the vulcanisation process (44). Acetone extraction of thiuram disulphide vulcanisates results in a large increase in relaxation rate, which is believed to be due to the removal, during extraction, of ZDC which acts as an antioxidant. Also of interest is the observation that zinc and ammonium dialkyl dithiophosphates are as effective as ZDC (45). Butyl xanthogen disulphide may be used as a 'sulphurless' vulcanising agent to yield products of improved ageing properties, provided that zinc diethyldithiocarbamate is added to the mix (46).

Detailed stress relaxation studies have shown that sulphurless vulcanisates (TMTD, dicumyl peroxide) degrade by an autocatalytic process which is retarded by classical antioxidants, and this may be a case of random chain scission (47). Sulphur and accelerated-sulphur vulcanisates, however, appear to degrade by a mechanism that may involve cross-link scission. A stress-relaxation study of radiation-cured natural rubber shows that, unlike accelerated-sulphur vulcanisates, no appreciable cross-linking occurs during relaxation (48).

Ozone cracking and antiozonants (49) continue to be topics of investigation and evaluation. One report (50) serves to stress the difference in mechanism between ozone attack and oxidation. Some of the best antiozonants (substituted *p*-phenylenediamines) are the least active antioxidants and, conversely, the best antioxidants are the least active antiozonants. Another report (51) based upon stress-relaxation studies of natural rubber and SBR black mixes, suggests that *N,N'*-disubstituted *p*-phenylenediamines and substituted hydroquinolines function by different mechanisms. Studies on SBR-black mixes have shown (52) that both of these classes of antiozonants are rendered more effective when they contain electron-repelling groups, and this conclusion is supported by the results of a chemical screening test for antiozonants with cyclohexene as a model substrate (53). The suggestion (54) that ozone is specifically necessary for flex cracking is not borne out by the report (55) that dicumyl peroxide produces cracking, provided that it is incorporated in the rubber mix and is irradiated by ultra-violet light. It now appears, therefore, that cracking may be induced by free radicals, even in the absence of ozone.



**Synthetic rubber***Styrene-butadiene (SBR)*

Although recent interest has been centred mainly on aspects of vulcanisation, one study (56) investigates the effect of ethylenediaminetetra-acetic acid (EDTA) in the ferrous-activated sulphoxylate type of system used in the low-temperature hydroperoxide-initiated preparation of cold SBR. Conversion is unaffected by the EDTA/ferrous ratio provided that this is greater than one. The demonstration (24) that sulphur reacts with olefins by a polar mechanism has been followed by an attempt to elucidate the broad path (polar or radical) by which various accelerated-sulphur systems vulcanise SBR gum-stocks (57). The technique used consists of adding a series of chemical 'mechanistic probes' to the mixes and noting their effect on the rate of cross-linkage formation (measured by equilibrium swelling). Hydroquinone and 1,1-diphenyl-2-picrylhydrazyl are typical of the probes used. These are well-known free-radical acceptors which inhibit or markedly retard free-radical reactions. Their effect on polar reactions, on the other hand, was expected to be comparatively minor. The investigation indicated that DPG-sulphur vulcanisation proceeds by a polar mechanism. TMTD-, ZDC- and MBT-sulphur vulcanisation proceeds by mechanisms that are predominantly polar, benzthiazolyl disulphide (MBTS)- and sulphenamide-sulphur vulcanisations proceed by mixed polar and radical mechanisms and radiation vulcanisation proceeds by a radical mechanism. Results with a 'sulphurless' TMTD system were inconclusive.

Studies on SBR gum-stocks and tread-stocks have shown that by replacing the thiol hydrogen of MBT by a diethylaminomethylene group, a fast cure without delayed action is obtained (58). Replacement by a diethylamino or morpholine group results in a delayed-action effect (59) and therefore improved scorch resistance. DPG or hexamethylenetetramine used in conjunction with benzthiazole- and thiuram-accelerated systems show synergistic activity and a radical mechanism is proposed (60). A mixture of morpholine disulphide or piperidine disulphide with MBTS provides a 'sulphurless' system with excellent scorch properties (61).

*cis-Polybutadiene*

The polymerisation of butadiene by lithium butyl in hydrocarbons gives a product that is ~90% of the 1,4 form. As already stated above, polar impurities, present during isoprene stereospecific polymerisation, result in increased non-specificity by forming a complex with the lithium, and similar effects have been found during the stereospecific polymerisation of butadiene (62). The use of aluminium tri-isobutyl with titanium tetrachloride gives 90% of the 1,4 form, and although the system can be

adjusted to obtain 98% of the *trans*-1,4 isomer, it was not found possible to obtain more than 60% of *cis*-1,4 isomer with this system (63).

The physical and service properties of *cis*-1,4-, *trans*-1,4- and atactic-1,2-polybutadienes and their copolymers have been reported (64), and are of great interest. The tensile strengths of gum-stocks of copolymers are low (~300 p.s.i.) but increase abruptly when the proportion of a single structural type exceeds 90%, becoming maximal at 100%. Thus, gum-stocks based on 100% *trans*-1,4, *cis*-1,4 and atactic-1,2 polymers possess tensile strengths of 3200, 2500 and 600 p.s.i., respectively. Evidently the orientated crystallisation which occurs during extension, and which leads to high-strength properties, is only achieved by polybutadienes of virtually a single structural type. Resilience and heat build-up of *cis*-polybutadiene tread stocks are said to be at least equal to those of natural rubber.

It is evident that this polymer is being actively developed in the U.S.A. both as a passenger-tyre rubber and, when blended with natural rubber, as a truck-tyre rubber. This tendency reflects the increased security being sought by rubber processors in a tyre-rubber whose price and availability are independent of economic and political factors beyond their control. This is now possible by the availability of butadiene monomer in virtually unlimited supply.

#### *Butyl*

The comparatively short life of butyl tyre-curing bags made with vulcanising systems based on sulphur has led to the development of special phenol-formaldehyde (P/F) resin vulcanising agents which are now widely used in the tyre industry. These resins are slow in curing, but cure may be greatly accelerated by a hydrated stannous chloride additive (65). Another important development (66) has been the replacement of sulphur by morpholine disulphide in a TMTD-accelerated system where low reversion and good ageing properties, at least equal to that of P/F systems, are claimed. The use of tellurium methyloctyldithiocarbamate and ethyleyclohexyldithiocarbamate is also claimed to improve the ozone-resistance of steam-cured butyl products, by virtue of their increased hydrophobicity (67). A novel development is that of 'attrited' carbon blacks (treated by milling) which, it is claimed (68), give butyl products of high tensile strength and elongation, and reduced modulus and heat build-up (69). A butyl latex is now available in the U.S.A. (70).

#### *Special-purpose rubbers*

Raw acrylonitrile-butadiene rubber (NBR) is very 'nervy' and difficult to plasticise for processing, since it hardens on milling. By

treating NBR latex with an iron salt and dimethylphenyl-*p*-cresol and then coagulating, a dry rubber is obtained which may be plasticised by hot-air treatment at 140° (71).

Kinetic studies on the thermal vulcanisation (72) of NBR suggest that the process is one of thermal polymerisation between pendant vinyl groups of the polymer. It is accelerated by MBTS, but the supposed demonstration that the accelerating effect is linearly related to the square root of the MBTS concentration is incorrect, since in fact it is first-order with respect to MBTS. Kinetic studies are also reported of the sulphenamide- and DPG-accelerated sulphur vulcanisation of NBR (73).

The special techniques necessary to cure polyurethane rubbers can be avoided by use of dicumyl peroxide and conventional mould methods (74). Improved dynamic properties are claimed, although tear strength suffers. An interesting study has been reported (75) using a polyether-based polyurethane containing pendant hydroxyethyl and *n*-propylene groups. This polymer was cured with 2,2'-dimethoxybiphenyl 4,4'-di-isocyanate which reacts quantitatively, and it has been shown that cross-link intensity values determined chemically are in excellent agreement with those determined physically using equilibrium compression modulus values. This result is gratifying but surprising since differences due to chain-entanglements would be expected.

Several chemical modifications of dimethylsilicone rubbers have been reported and discussed from the point of view of the enhancement of a particular property. The presence of occasional phenyl groups gives improved flexibility at low temperatures. Pendant vinyl groups permit the use of less reactive peroxides for curing (76), and the pendant *n*-cyanopropyl groups improve both the low-temperature flexibility and the solvent resistance of the polymer (77). A silicone polymer containing fluorine (poly-trifluoropropyl-methylsiloxane) has been synthesised and found to be highly resistant to fuel oils and chlorinated solvents (78).

### Analytical

A convenient method of determining MBT, zincMBT and MBTS in rubber extracts by amperometric titration with silver nitrate has been described (79) and a method of determining MBT by iodine titration is now published (80). Di-*o*-tolylguanidine dicatechol borate can be detected in cured rubber by the appearance of a light blue colour on treating the acetone extract with sodium hydroxide solution (81). Useful chromatographic methods are described for the estimation of elemental sulphur in accelerators (82), and of trace amounts of copper in rubber (83). The use of copper oleate as a chromatographic colour reagent is suggested for estimating ZDC in rubber extracts (84).

An X-ray diffraction method for estimating free zinc oxide in vulcanised rubber should prove useful (85). Ebonite which contains whitening gives erroneous ash values because of calcium sulphate formation, but improved results can be obtained by ashing first at 400° and finally at 900° (86).

A notable advance in infra-red spectroscopy (87) is the use of a special grating spectrometer which reduces scatter due to carbon black and thus allows a direct examination of black stocks. Such an instrument is not widely available, however, and those with commercial instruments will find helpful a collection of spectra of the pyrolysates of most common rubbers (88). It must be noted that the 11.3  $\mu$  absorption band, usually associated with 3,4-polyisoprene structures, may not in fact be due to it. It has been suggested that a band at 1.64  $\mu$  can be more reliably used diagnostically for this type of structure (89).

A convenient spot-test for natural and synthetic polyisoprenes (90) is based on chromic acid oxidation and the identification of the acetic acid formed, using lanthanum nitrate and iodine. The use of perbenzoic acid for microstructure analysis of polybutadienes has now been extended to polyisoprenes with results that agree very well with those obtained by infra-red spectroscopy (91). A rapid spot-test has been developed for differentiating between polyester and polyether urethane polymers (92); a simplified colorimetric method for determining bound styrene in SBR should find increasing use (93).

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## LEATHER

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THE number of papers on leather chemistry published over the last two years has continued to increase. The growing interest in the physical properties of collagen and leather is emphasised by the volume of work published in this field, while the chemistry of collagen and other skin components has also lent itself to extensive studies. In the realm of practical tanning, zirconium continues to provide good research material as well as tannages based on glutaraldehyde and di-aldehyde starch. Work on sole leather continues to focus mainly on the techniques of rapid tannage. In view of difficulties that may be faced in the future, this report includes a short account of the work done on effluent disposal and waste product recovery.

### Collagen

In the past two years a great many papers have been published dealing with the chemical and physical properties of collagen. The work by Morgan & Mitton (1) on the physical properties of collagen and tanned collagen fibres is the outstanding contribution made in the latter field.

The treatment of collagen with  $\gamma$ -radiation (2) was shown to reduce the shrinkage temperature and increase water solubility. Radiation sterilisation (3) has been suggested as a possible curing method of the future. The behaviour of hide substance subjected to heat in the presence of small amounts of a diluent (4) has been likened to the depression of the melting point of a crystalline substance by an impurity, and shrinkage temperature is explained on this basis. From heats of melting and specific volume Ghosh (5) puts the crystallinity of collagen between 70% and 80%.

Collagen swelling (6) continues to create interest and Frazer & Macrae (7) suggest a possible rôle for water in the collagen structure.

Colour reactions and stains for proteins (8) and amino-acids (9) have appeared regularly with other analytical techniques applicable to collagen chemistry. Deasy (10a) described methods of purification of collagen and later (10b) the isolation of a compound of carbohydrate nature related to sialic acid. Sialic acid has also been found in cartilage and other connective tissue (11).

The esterification of collagen with methanol and ethyl chloroformate resulted in an increase in amino-nitrogen attributed to an N-O acyl migration in the serine and threonine residues (12a). The same authors showed that the N and C terminal amino-acids of collagen, procollagen and reticulin were identical (12b).

The isolation of a tripeptide of structure L-L-N- $\epsilon$ -(glycyl- $\alpha$ -glutamyl)lysine (13) suggests that possibility of macro-loops along the collagen chain, although this peptide may have arisen in a side-chain reaction. Other tripeptides of importance in sequence studies (14) have also been isolated. Improvements have been made in the colorimetric determination of elastin (15) and Ornes & Roddy (16) describe methods of isolation and staining of elastic tissue and their subsequent use in determining the modification of elastin during the processing of skin to leather.

### Animal skin, curing and fungicides

Green (17) describes with illustrations some hide and skin curiosities found in Kenya, including those attacked by tick-bird, ants and moths. O'Flaherty (18) reviews the life history and effect of the cattle grub on animal and leather while Dempsey (19) considers hide damage by warble and gives an account of recently introduced systemic insecticides and their possibilities for future use.

Hides cured with salt containing soda ash and naphthalene (20) showed no red heat or maggots and remained in good condition during storage. Losses in weight (21) up to 5% in green hides have been reported when sodium carbonate was added to salt. The use of 2% paludrine (22) added to salt stopped red heat, and a 1% solution used for 10 hours prevented hair slip and putrefaction for one month. Additions of 0.5% to the soak inhibited putrefaction for 4 days. A series of insecticides was examined (23) to see if they stained leather, but there were no visible stains attributable to the insecticides after fat liquoring.

Hauck (24) suggests that the measurement of specific gravity would be a quick way to determine the salt content of cured hides.

Fungicidal effects of organo-mercury compounds (25) have been investigated and compared with those of well-tried fungicides, e.g., sodium pentachlorophenate; whereas the latter requires 1 part/15,000 for effectiveness, the mercury compound requires only 1 part/200,000.

Green (26) has reviewed the methods of comparing fungicidal properties and of assessing the effectiveness of mould-proofing treatments and describes a new test method.

### Pretanning

Much of the interesting work in the pretanning field continues to centre around enzyme unhairing. The difficulties experienced in



the removal of fine hairs and the inconsistency of results obtained with enzymes (27) have been discussed and work is being continued to determine the extent to which leather quality depends on the nature of the enzymes employed. Dhar & Bose (28) report that by a comparative assessment, the leathers manufactured by unhairing with microbial proteases and lime showed no consistent differences.

Green & Mitton (29) described experiments on the bating conditions in glacé kid production: the results indicate that a wide variation in bating conditions produces little difference in the overall quality of the finished leather. Previous work (30) on bates aroused comment and criticism (31a), especially with regard to the progelatin theory. Future methods of bating suggested by Grimm (31b) include soaking back dry hides with enzymes, thus dispensing with the need for a separate bate and the removal of non-collagenous matter and scud with alkyl sulphates or substituted amino-carboxylic acids. The latter method requires a short bate.

The importance of chemical changes in collagen and other hide components under conditions of liming and bating and their relation to loss of hide substance are discussed by Hörmann & Schubert (32).

### Vegetable tannage

The recent advances in the chemistry and biochemistry of commercially important condensed tannins (33) and their importance in relation to certain aspects of leather chemistry, including redness of vegetable extracts, identification of condensed tannins in leather and reaction with bisulphite, are discussed by Roux.

With regard to hydrolysable tannins a possible mode of biosynthesis (34) has been considered as the result of a new theory of alkaloid biosynthesis (35). Hathaway & Seakins (36) have isolated and identified two hydroxystilbenes from *Eucalyptus wandoo*; a second occurrence of *Hamameli* tannin (37), this time from the Spanish chestnut, has been shown to be identical with the natural product previously isolated from *Hamamelis virginiana* (38). The synthesis of brevifolin has been described by Wanzlick (39) and Freudenberg (40) has investigated the biosynthesis and constitution of lignin.

On the more practical aspects of vegetable tanning the uses of di-aldehyde starch as a pretanning agent (41) and ion-exchange membranes (42) for controlling the pH of tanning liquors have been considered in relation to rapid sole leather tannages. A closed circulating system for rapid sole leather tannage has been described by Shuttleworth (43) and Atkinson & Cutting (44) have discussed methods of rapid tannage for light leather production. An improved catechol leather is produced by the action of an aqueous

solution of ammonia or gaseous ammonia followed by fumes of formaldehyde (45).

Evelyn (46) reports from work on wattle extracts that the diffusion of polyphenols into hide is inversely related to the molecular weight of the tannins. When the results are corrected to the same degree of swelling the sorption of polyphenol is inversely, and the 'fixed tannins' directly, related to the molecular weight. The total sorbed matter is independent of molecular weight. The importance of swelling in the fixation of tannins has been confirmed by Sykes (47). Results obtained indicate that hydrothermal stability is dependent on the amount of tannin fixed rather than on the fixation of mimosa tannin at any particular site in the collagen.

### Chrome tannage

Chrome tanning processes with 33% and 50% basic liquors are described (48) in which all the tanning material is added immediately after the pickle acid. The resulting leather has good substance, uniform distribution of chromium oxide and firm flanks. Chrome-tanned leather with fuller flanks and tight, smooth grain is claimed to result from a pretreatment with phosphate glass (49), while increased drumming and chrome uptake give a soft leather (50).

Gustavson (51) describes a chrome-alum tannage in which the acid-binding faculty of collagen is utilised for the formation of basic chromium sulphate *in situ*. The chrome alum is applied in definite proportions and is dissolved by the moisture in the pelt, so that subsequent tanning takes place entirely within the pelt. A practically boil-proof leather is obtained.

Shuttleworth & Sykes have investigated the mode of co-ordination of amino-acids with cationic chromium in acid aqueous solutions by spectrophotometric (52a) and potentiometric techniques (52b). From the results of spectrophotometric studies the extent of co-ordination appears to be proportional to the  $pK'$  values of the carboxyl groups which are themselves influenced by the number of C-atoms separating the carboxyl and amino groups. Thus  $\epsilon$ -amino-acids are better complexing agents than are  $\alpha$ -amino-acids, and the resulting complexes formed by  $\epsilon$ -amino-acids and chromium sulphate are more resistant to penetration by the carboxyl residues of collagen and therefore less efficient as tanning agents than the complexes with  $\alpha$ -amino-acids. These results were confirmed by tanning trials using isomeric forms of amino-n-butyric acid.

The neutralisation effect of a series of alkalis on the properties of finished leather were investigated by Stubbings (53) and compared with the results for sodium bicarbonate. If the alkalis were added

slowly and in equivalent units by titration, results similar to those with sodium carbonate were obtained. Pre-neutralisation with calcium formate (54) followed by sodium carbonate or sodium sulphite gives milder deacidification and more rapid penetration to the inner zones than either carbonate or sulphite alone.

### Other tannages

Zirconium tannage has been reviewed by Williams-Wynn (55), particular attention being given to practical aspects of tanning, and also by Somerville (56), who considers zirconium salts for premium white leathers and retannage of chrome side leather.

The particle size of zirconium has been shown to be a major contributor to the rate of penetration of zirconium into hide (57). Rapid penetration was found to take place by performing a dry tannage after normal pickle. Under these conditions zirconium had the smallest particle size. The factors affecting the particle size of zirconium chloride affected zirconium sulphate in a similar manner. A brief description of the tanning and finishing of 'Supra', the French patented (58a) zirconium-tanned leather, is given by Paquet (58b).

A patent has been granted for tanning with iron salts (59), which it is claimed gives a leather superior to that obtained by the conventional iron tannage. The skins are first treated with a non-basic or weakly basic, trivalent iron salt mixed with equivalent amounts of dichromate, and are tanned by the addition of a reducing agent which converts the original salt into a basic tanning salt inside the pelt. Better results are obtained by partial replacement of the iron salts by chromium and/or aluminium salts.

The tanning properties of malonaldehyde and succinaldehyde have been investigated (60) and Simoncini (61) describes recent work on the tanning action of chlorinating agents such as chlorine water, hypochlorous acid, sodium hypochlorite and sodium chlorite.

The results of tanning with glutaraldehyde (62) show that the leather produced has superior properties to formaldehyde- and glyoxal-tanned leather. Under certain conditions maximum shrinkage temperature is reached in 1 hour and complete exhaustion of the tanning liquor is possible. No difficulty was experienced in the post-tanning treatments and the finished leather showed high resistance to perspiration and soap solution and was of a soft and pleasing character.

Sykes (63) describes a process of leather manufacture in which raw hide is frozen and the water in the fibre matrix is turned to ice. The ice is sublimed at 10°F in chilled dry air and the raw hide treated with silicone oils. The resulting leather has many properties to enhance it.

## Post-tanning treatments

### *Dyes and dyeing*

The tanning and detanning action of dyes has been investigated by Otto (64). The retannage of chromed skins with sumac, gambier or equivalent syntans (65) has been shown to give excellent properties to materials subsequently dyed for gloving leathers. Fluorescent oxadiazole compounds (66) which are practically colourless have been recommended for addition to dyebaths for brightening purposes and to improve optical properties. Recent progress in the field of dyestuffs for leather is discussed by Nursten (67).

### *Fat liquoring*

Mattei & Roddy (68a) have explored the use of fish oils for fat liquoring. Ocean perch, herring, salmon and menhaden (68b) oils gave results similar to those obtained by fat liquoring with cod oil, although the latter oil gave a softer surface to the leather. A method for the sulphation of highly unsaturated oils is described (68c). The influence of the type of oil, degree of sulphation and neutralisation levels of fatty acids on the physical properties of upper leather (69) have been investigated, as well as the fat-liquor distribution in chrome-vegetable combination tanned side leather (70).

### *Finishing*

The properties of ten synthetic resin dispersions (71) have been reviewed and also compared in simple pigmented finishes. The yellowing of white leathers (72) is ascribed to traces of iron, manganese, copper and lead in the white pigments used in finishes.

Leathers finished with a polymer dispersion containing carboxylic groups in the presence of a zinc compound (73) are said to show fastness to hot ironing up to 300°. Recent developments in the chemistry and technology of polyurethanes (74) are discussed and the effect of the composition of urethane films on such properties as colour and gloss retention are described.

### *Waterproofing*

Much patent literature has been concerned with waterproofing and patents have been granted for this purpose for organo-silicon-chromium co-ordination compounds (75) (also as tanning agents) and hydroxyl-containing chromium co-ordination complexes of perchlorofluoromonocarboxylic acids (76). Silicones are also used considerably.

Only limited success has been had with finding a surface treatment for vegetable-tanned sole leather (77) and filling seems to be still the best method for such leathers. Full-chrome leathers can be

successfully treated but they require 10% of the agent on leather weight for effectiveness.

### Tannery waste

The American Leather Chemists' Association (78) have proposed methods for analysis of industrial wastes, including determination of dissolved oxygen, bacterial oxygen demand, residue, pH, organic nitrogen, sulphide and chloride. The self-purification of tannery effluents has been considered by Ludvik & Jansky (79).

In Japan (80) hide fleshings not used in gelatin factories have been converted into cattle and poultry feeds by cultivation of *Rhizopus fungi* by the koji fermentation process. Patents have been taken out for the recovery of chromium from spent tanning liquors (81) and leather waste (82a), and the production of emulsifiers, soaps, etc., from animal glues and other protein hydrolysates (82b).

The manufacture of reconstituted leatherboard (83) from scrap leather and latex has been described.

### Testing and analysis

Bowes (84) points out that total nitrogen is not necessarily a true indication of total protein present and that a more desirable method of determination of hide substance is required, and for this the determination of hydroxyproline is suggested. Results obtained by this method are 5–10% lower than by the conventional Kjeldahl method. This new method might also be used for detecting other nitrogen-containing substances in leather such as dimethylurea. Kubelka (85) has put the nitrogen content of steer hide at 18.0%, as opposed to the present accepted value of 17.8%. This difference changes the conversion factor of nitrogen to limed hide from 5.62 to 5.56.

The determinations of overall basicity and chromium oxide content (86) of chrome-tanned leathers have been reviewed and sources of error and methods by which the reliability of the analyses can be improved are discussed.

Küntzel & Kröll (87) have investigated the methods of determining ash in chrome leather and the resulting behaviour of the chromium compounds. They conclude that the sulphated ash method of the Society of Leather Trades' Chemists cannot be used because on prolonged ashing, up to 24 hours,  $\text{SO}_3$  is lost from the chromium salt and a low ash figure is returned. Ashing at 800° of wet oxidation and subsequent drying at 400° appear to be the best methods.

Kubelka (88) has proposed a factor of 2.76 for calculating chrome tannin from the chromium oxide content of the leather. Results so calculated are in good agreement but are slightly higher than those calculated from the formula of Kanagy (89), viz., chrome complex

(chrome tannin) =  $2.09 \text{ Cr}_2\text{O}_3 + 2.78$ . It is suggested that tanneries should calculate a factor for the particular type of leather being produced and that this factor would be sufficiently accurate for control work.

Morgan & Mitton have published a great deal of work on the mechanical properties of collagen and collagen-tanned fibres (1) and in conjunction with Barnett (90) have described a shrinkage temperature apparatus capable of taking up to 32 samples and raising the temperature to  $125^\circ$ . Change of shrinkage temperature as a criterion of tannage (91) has been briefly considered and shrinkage temperature has also been used to give a date to the Dead Sea Scrolls (92).

It has been suggested that strength qualities of leather can be adequately judged by the tongue tear test (93), while Toth (94) uses a microphone placed near a leather under stress to hear the fibres breaking. By this method fibres can be heard breaking at  $2/5$ ths of the normal load. A number of new physical testing methods have been adopted by the International Union of Leather Chemists' Societies (95).

Bowes & Moss (96), from tests with lactic acid, infer that the higher the chromium content the longer leather will resist the action of perspiration. Other workers conclude that the measurement of water absorption (97) can be made the basis for comparing the perspiration resistance of leathers.

Problems in devising fastness tests for leathers are considered by Landmann (98) and the physical measurement of colour (99) with reference to quality of illumination, reflection, behaviour of object, and eye characteristics is discussed by Derbyshire; potential value of colour measurements to industrial users of colour is also considered. Davies & Nursten (100) have put forward a provisional method for the testing of the fastness of coloured leathers to dry cleaning.

A direct-reading instrument for moisture determinations (101) based on the principle of change of dielectric constant and resistivity is described for tannery use.

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**FIBRES, PLASTICS, PAINTS, Etc.**



## PULP AND PAPER

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THE release of details of the Inverform machine for board and paper making, the inauguration of Sudbrook Pulp Mills (1), employing a Kamyr continuous digester to produce bleached pulp from mixed hardwoods, a Symposium on the Fundamentals of Fibre Attraction and Bonding, and the Eucepa conference on statistics in May 1960, are some of the important events during a two-year period, which, in general, saw continued mill expansion and modernisation, the growth of pulp and paper mills in under-developed countries, and intensified research and efforts to elucidate the basic principles governing the paper and board making processes and the characteristics of the products obtained.

### Fibrous raw materials and pulping

In 'A search for new fibre crops', Nieschlag (2) has described a scheme for evaluating the potential use as papermaking fibres of a large number of materials, taking into account botanical characteristics, chemical composition, fibre dimensions, yield after sodium chlorite maceration and qualitative physical and visual appraisal. This was applied to 58 plant species representing eleven families. Tamolang (3) has published further data on the fibre dimensions of Philippine broadleaved and coniferous woods, palms, bamboos and grasses.

The use of modified cotton linters has attracted some attention (4). Harpham *et al.* (5) have described the fine paper properties of different cuts of commercial linters and the chemical modification of second cut linters to a low degree of substitution by cyanohydroxyethylation, carboxymethylation, hydroxymethylation and hydroxypropylation reactions. Hydroxyethylated linters handsheets (D.S. 0.18) had twice the burst, 1.2-1.3 times the tear and 25-70 times the folding endurance of second cut linters sheets, depending on beating time. Hydroxyalkylation experiments (6) with linters are also reported, in which handsheets were prepared and Valley beating curves, sizing degree, porosity, moisture sorption and strength properties were evaluated; compared with purified linters, entirely different combinations of porosity and strength were obtained, the sheets being much more porous at the same tensile

strength or much stronger at the same porosity level. Spadaro *et al.* (7) have described cyanoethylation and hydroxyethylation studies with linters carried out at the Southern Utilisation Research and Development Division; cyanoethylation in this case yielded no appreciable improvement in properties, but hydroxyethylation led to folding endurance values of up to 14,000, while freeness decreased to 115 with a beating time of 2 h., compared with a folding endurance of 500 and a freeness of 220 in a control sample beaten for 3 h. Hydroxyethylation and other chemical modification studies at the Institute of Paper Chemistry have been discussed by Ward (8).

Some preliminary data on the Fibre Activator Process have been published by Michigan Research Laboratories (9). This process is concerned with the 'conditioning of cellulose and other fibres by undisclosed chemical means', which is said to result in the liberation of bound water in the fibres; at the same time the treatment improves retention and facilitates the addition of chemical additives and resins. Latex retention can apparently be achieved without acidification or use of alum at pH 3-10. It is further claimed that the stock is faster drying and that all strength properties, opacity, formation and printability are improved.

In the mechanical pulping field the search for improved grinding methods is being continued. At the third International Mechanical Pulping Conference, Bersano (10) described the development of a new type of grinder, in which the logs rest on a pair of horizontal longitudinal supporting rolls and are ground by a series of conical grinding wheels set at an angle to the log, which cause the log to rotate and move longitudinally. The grinder acts by compression of the wood with subsequent pulling away of the fibres and chemical treatment can be included. Groundwood of good burst and tear strength and opacity or bundles of fibres suitable for further processing can be produced. Less power is consumed than with conventional grinders. At the same conference Hoholik (11) reported on coarse grinding followed by refining, and presented data to show that the mechanical pulp produced is equivalent or better in quality than those made completely by grinding at the same total power input. D'A. Clark (12) has described a new approach in groundwood evaluation; it is suggested that replacement of the present system of testing (freeness, burst and tear strength and specific volume or density) or at least supplementing by a much more fundamental fineness-length-cohesiveness system, would give a clearer insight into the properties of groundwood.

Crosby & Coe (13) have described the Hifibre Process for hardwood pulping with lime in place of soda. Steeped chips enter a roller mill, where they are compressed; they are then further treated with chemical and defibred in a koller mill. The unbleached pulp obtained is said to show good opacity.

Multistage cooking and modified sulphite cooking continue to receive notice. A very useful review of the former has been presented by Rydholm (14) who subdivides the various processes into (1) those finishing with an acid sulphite cook and (2) those finishing with an alkaline cook. The first group comprises the Skutskar process (15) in which pine is cooked with sodium sulphite/bisulphite liquor at pH about 6 followed by injection of sulphur dioxide. These modifications overcome the difficulties arising from the heartwood constituents and phenolic compounds in various conifers; moreover, glucomannan stabilisation makes two-stage cooking of interest not only for woods with phenolic constituent but for all types of softwoods; in hardwoods the glucomannan content is not sufficiently high to offer advantages when adopting this procedure. A comparative study of spruce pulps prepared by (a) a two-stage method using sodium monosulphite (pH 9-10) for the first stage followed by an acid sulphite stage, (b) a single stage sodium bisulphite cook (pH 4-4.5) and (c) a single-stage calcium sulphite cook employing very mild cooking conditions has been reported by Vethe *et al.* (16).

Two-stage cooking finishing with an alkaline cook, of special value for dissolving pulps, can also be used for papermaking pulps. A modification with lignin removal shifted to the sulphite stage is the Sivola sulphite-carbonate process (17), which gives pulps with  $\alpha$ -cellulose contents of 87-97%; for paper pulps the bisulphite-carbonate cook is probably preferable. The carbonate stage modifies the properties of the bisulphite pulp in such a manner that only part of the hemicelluloses are removed and, in special cases, where the bisulphite stage is interrupted very early, pulps approaching sulphate pulps in strength can be obtained. Freedman (18) has compared a two-stage soda cook for hardwoods with kraft cooking and found that not only are the two-stage soda pulps stronger than conventional soda pulps but that their strength is of the same order as that of kraft pulps or even better; this process also yields considerable savings in causticising costs.

Calcium-base, high-yield sulphite pulping is now being practised in a number of Canadian mills producing newsprint pulps. A detailed description of plant lay-out and mill operation has been given by Lambert (19) together with a discussion of the economics of the process. The freeness of the high-yield stock as supplied to the machine is 620-640 c.s.f. or 40-50 points below that of normal low-yield pulp, while the printability of the paper as evaluated on a Vandercook proof press usually shows a loss of only 1.5%, although in some cases no difference has been noticed when changing to high-yield operation. High-yield acid pulps are also of interest for corrugating medium.

Engelhardt *et al.* (20) have reported on high-yield sulphite cooking experiments with special reference to vapour-phase cooking

and Zirngibl (21) has compared normal cooking with sodium bisulphite, vapour-phase cooking with sodium bisulphite and digestion with a mixture of sodium and calcium bisulphite.

Schwabe & Abdelmoniem (22) found that unbleached aluminium bisulphite pulp showed good colour and strength, could be beaten easily and was readily bleached, yielding pulps of high  $\alpha$ -cellulose content; novel bulky pulps could also be produced. Advantages cited are: liquor recovery simple, risk of blackening of pulps during cooking reduced and scale problem eliminated.

Rydholm & Lagergren (23) have discussed the rate-determining delignification reaction in technical sulphite cooking from kinetic and lignin chemistry viewpoints, and Ingruber (24a) has reported on a study of the influence of the pH factor in the process. The same author (24b) also investigated the pH changes in dilute solutions of strong acids and alkalis in the pH range 2-12 when various wood species were introduced and compared the pH development in pulps such as sulphite and kraft pulps.

Jensen *et al.* (25) have examined the possibility of using radioactive tracers to follow the penetration of calcium-base sulphite cooking liquor into wood. The use of radio-isotopes in cooking investigations is also being studied at the British Paper & Board Industry Research Association.

In the alkaline pulping field sulphidity control is effected with elemental sulphur (26), and Peckham & May (27) cooked southern pine with an alkaline liquor rich in polysulphides and obtained a pulp with a screened yield advantage over the kraft pulp of up to 2% based on moisture-free wood, and the colour and bleachability of the pulp compared favourably with the conventional pulp. Scopp Associates (28) have claimed unprecedented yields with the use of polysulphides in kraft pulping. Swartz *et al.* (29) have described the system at Bowaters Southern Paper Corp. where sulphuric acid is used for sulphur make-up to permit recovery of spent cold caustic pulping liquors, to increase the sulphidity of kraft cooking liquor and to maintain liquor sulphidity at a desired level.

Potassium-base kraft pulping has been described by Nepenin & Vybornova (30), who claim that the substitution of potassium for sodium accelerated the cooking process and that the  $\alpha$ -cellulose contents were higher by 2-4%. Furthermore, the pulps were beaten more easily and had improved mechanical strength properties.

### Stock preparation

There is some doubt regarding the practicability of ultrasonic treatment of papermaking stock as an alternative to beating, so that an extensive investigation by Jayme *et al.* (31) of changes in

the colloid chemical properties of cellulose fibres as a result of high-frequency and ultrasonic treatment is welcome. Reference is made to commercially available equipment such as the Escher Wyss shives remover, the Supratonator, the Ultra Turrax and the Polytron equipment. Willems (32), inventor of the Fibrotom, also reported on this subject to the A.T.I.P. conference in November 1959.

Many different methods for evaluating the beating effect, including determinations of filtration time, filtration resistance, specific surface and volume, Jayme water retention value, initial wet strength, fibre length and viscosity measurements, have been critically compared by Nordman & Aaltonen (33) and Kane (34) has developed a mathematical expression for the variation of fibre length distribution during the beating process, and has similarly analysed the relationship between beating influence, fibre length and tensile and tear strength. Arlov (35) has compared the fibre strength and bonding behaviour of fibre fractions obtained from pulps beaten in a P.F.I. laboratory beater and in two industrial beaters, one with basalt tackle, the other with metal bars (see also Vinetskaya, reference 36).

Ingmanson & Andrews (37) found that filtration resistance of pulps increases exponentially with beating time and that for a whole pulp it depends primarily on the amount of fines and fibre debris produced. Bulk compressibility increased in direct proportion to increases in specific volume with refining time, hence as fibre swelling increases with beating it is to be expected that in a wet-pressed sheet there will be more fibre-to-fibre contacts as beating proceeds with resulting higher strength characteristics.

Rapson *et al.* (38) have measured the colour and brightness reversion of pulps during beating experiments in a Valley beater; drop in brightness is attributed to increased surface area developed by mechanical action.

### Papermaking

The Inverform machine (39) at St. Anne's Board Mill is undoubtedly one of the most important developments in paper and board making. This will be realised from the fact that pilot machines have been run at speeds of 800 to more than 2000 ft./m. when making multi-ply board, and that a single-ply experimental machine, 14 in. wide, has been run at speeds up to 5000 ft./m. The limitations to the speed of water removal from wet webs, particularly heavier paper and board, are overcome by the use of a number of top wires and the upward removal of water. Flow box consistencies range from 1 to 1.8%, considerably higher than with conventional cylinder mould machines. The strength properties of the sheet obtained compare favourably with those for a normal



cylinder machine, while the sheet properties in the machine and cross direction are more uniform; ply adhesion and bulk are improved.

Stock flow on to the wire, sheet formation and factors affecting sheet transfer from the wire on to the press section have been investigated further. Lamb (40) has suggested a mechanism for spouting or stock jump, which can occur on high-speed Fourdrinier machines and concluded that spouting is best described as a splash resulting from non-uniform flow impinging on the wire, inception of spouting being largely dependent on geometric conditions. Mardon and his colleagues (41) have analysed the wake effect, ridge formation and spout development on the wire of Fourdrinier machines and shown photographs of these disturbed conditions. Yih & Spengos (42) have investigated the growth of disturbances over and downstream from the table rolls and have presented a new analysis of the formation of rings from a thin layer of fluid attached to and rotating with the table rolls.

Campbell (42a) has advanced a theory to explain sheet take-off at an open draw couch and interpreted the action of the suction couch in terms of a film of water forming between sheet and wire after the trailing sealing strip is passed; movement of the line of separation and the initiation of breaks are examined. Tardiff (42b) has dealt with the practical aspects of this study and discussed the operating factors which influence the efficiency and ease of the transfer of the sheet. Howe *et al.* (43) have compared the actual couch draw, i.e. the percentage difference in speed between the couch and the first press, on two paper machines with the theoretical elongation of this part of the paper web, calculated from measurements of the angle of take-off, the work of separation in lifting the web off the wire and the stress-strain properties of the web at the couch moisture content, while Woodard (44) has published a modification of the Howe method for measuring the force of stripping the web from the wire, together with some preliminary experimental results. Mardon *et al.* (45) have reported a study of the problem of the breaking and tearing of paper when it is removed from various surfaces in open draw, covering spot adhesion and skinning breaks; a theory of breaking and tearing is formulated and shown to give good agreement with experimental results. Radvan & O'Blenes (46) have studied web adhesion, using laboratory sheets which were pulled off a stainless steel plate at controlled angles at speeds approaching those on a slow paper machine; they also studied the initiation and spreading of tears and conditions governing the occurrence of self-healing breaks. Brecht & Führlbeck (47) used a specially designed tester to apply a sudden tensile stress to paper strips of varying moisture content and found that, independent of moisture content, the essential part of the stretch was effected almost immediately after the load was

applied. The practical implications of the results obtained were discussed with reference to the draws on paper machines.

Wilder (48) has studied the compression creep properties of wet pulp mats and correlated the results with an empirical compressibility equation, while Ingmanson *et al.* (49) determined the internal pressure distribution in compressible mats and compared experimental values of internal pressure drop with calculated values, based on static measurements of mat compressibility. The flow equations derived were used to determine the porosity distributions in fibre mats under fluid stress.

Wahlström (50) has reported an 18-month study of water removal and moisture distribution in a 1200 ft./min. newsprint machine suction press section in which detailed results were obtained on felt and paper properties and behaviour, and the influence of press nip conditions and other operating factors. As a result of this study a new theory of pressing is formulated and discussed. All the water that is removed from the paper is removed by compression in the in-going part of the nip, while in the out-going part water is transferred from felt to paper by capillary action. New methods for press evaluation are given.

One of the major sources of difficulties in converting operations, particularly printing, is the dimensional instability of paper when exposed to changes in atmospheric humidity, the usual remedy advocated being the correct conditioning of the paper under conditions approaching those to be expected in the press room. Brecht & Pohl (51) have now published an interesting study with an experimental conditioner similar to a Ross cycling plant with two chambers in which air of controlled humidity and temperature is blown against both sides of the web. From results on moisture uptake, shrinkage and stretching of the web, blistering and other changes in sheet flatness, it was shown that up to now there is no way of conditioning paper which renders it insensitive to changes in atmospheric moisture content. After a sufficient number of conditioning cycles a steady state is reached, when the conditioned paper exhibits less stretch on moisture absorption but greater shrinkage during drying, due to the release of dried-in strains. In conventional conditioning equipment not designed for humidity cycling the moisture applied helps to release the strains, but the conditioned paper can only be expected to lie flatter than unconditioned paper as long as atmospheric conditions catered for in the conditioning plant remain unchanged. Conditioning with an experimental atomiser in which the fine droplets penetrate into the paper very rapidly was also studied; development of such equipment would shorten the time required for conditioning. Hudson & Heinsius (52) also studied humidity and water cycling and the effects produced by stretching the damped paper in the cross direction with subsequent hot drying under slight pressure.

### Pulp and paper testing and properties

Fibre bonding is the fundamental mechanism underlying the papermaking process and much effort has been directed towards its elucidation. The knowledge gained and some of the many problems remaining were discussed at the Symposium on the Fundamentals of Fibre Attraction and Bonding sponsored by TAPPI (53) (Appleton, September 1959).

In a comprehensive discussion of work published on the physical nature of the fibre-to-fibre bond, van den Akker (54) considered the architecture of the bonds, as revealed by light- and electron-microscopy, the molecular nature of bonds, bond formation, methods for estimating bonded area and techniques for evaluating bond breakage during or following the application of stress.

Page & Tydeman (55) have developed a method for the direct observation of fibre-fibre bonds, based on the fact that areas of optical contact between fibres can be seen with polarised vertical illumination, provided difficulties arising from the light reflected and scattered from surrounding and underlying fibres are eliminated by dyeing part of the fibres to give maximum absorption of the light used. Strong evidence was put forward that these areas of optical contact form the fibre-to-fibre bonds responsible for sheet strength. The bonds observed were classified into (1) those showing complete optical contact over the mutual area of two crossing fibres (typical diamond shape), (2) those clearly prevented from bonding over the whole of the mutual area by the intervention of a third fibre, and (3) those which do not show optical contact over the whole of the mutual area between two clearly observable fibres, but for which incomplete bonding cannot be explained. The importance of the surface topography of the fibres and local plasticity is discussed. A study was also made of the behaviour of bonds in sheets under stress, which showed that both very gradual reduction of bonded area and extremely rapid fracture can occur. Some bonds were observed to diminish in size while under load at constant strain, while some partially broken bonds remained at constant area while the sheet was under stress at constant strain. The quite frequent occurrence even in unbeaten sheets of contact over virtually the whole area of crossing was noteworthy.

Jayne & Hunger (56) have continued their study of fibre bonding during drying, using steric electron microscopy. Thin-walled spring wood fibres were observed to collapse, but did not flatten out like ribbons, being shaped more like a double T-support; late wood fibres mostly preserved their original tube-like shape; the outer secondary wall showed wrinkles in an axial direction.

Thode & Ingmanson (57) have investigated factors contributing to sheet strength by ball milling a bleached sulphite pulp, fractionating the fibres and determining the specific surface and

swollen specific volume on the handsheets obtained by different methods. Only the filtration resistance method satisfactorily accounted for the large surface area contributed by the fines fraction in beaten pulps. While swollen specific volume was found to be directly related to tensile strength through fibre plasticising effects, the determination of surface area and of the distribution of surface between whole fibres and fines was considered useful primarily for establishing how most economically to achieve the desired strength properties through beating, refining and the use of beater adhesives. Based on the concept of a constant dry fibre area a revised method for estimating relative bonded area was proposed and sheet strength properties correlated with revised values for bonded area. The constancy of relative bonded area determined at different wavelengths of light was taken to imply that areas in optical contact may not be significantly different from actual bonded areas and that the assumption of linearity between specific scattering coefficient and fibre area is reasonably valid.

Swanson & Steber (58) studied the relationship between fibre surface area and bonded area and tensile strength for three other papermaking pulps of widely different characteristics. They confirmed the linear correlation between surface area estimated by light scattering and by nitrogen adsorption methods, first shown for a single pulp by Haselton. The proportionality constant relating the two properties was used for calculating the absolute bonded area of the papers; this area at various degrees of refining and wet pressing correlated with tensile strength. The data obtained indicated that bond density (bonding strength per unit bonded area) increases with the degree of beating. The assumption of Thode & Ingmanson of the constancy of the dry fibre surface area available for fibre bonding was found to be of doubtful validity for purified pulps.

Robertson (59) has reported on the changes in tensile strength, stretch and caliper when wet webs were progressively dried within the range 10-50% solids content. The water associated with the fibres was measured at the same time by different methods which yielded a measure of different portions of the associated water and the firmness with which the water was held by the fibres. A critical solids content which marks the disappearance of 'free' water was found and a distinct difference was observed in the behaviour of virgin pulps and pulps which had previously been dried. The preliminary results reported suggest that the fibre properties which contribute to wet web strength may be assumed to be hydrodynamic specific volume of the fibres, specific surface, flexibility, fibre length and delignification.

Brecht & Erfurt (60) have described a new tester for determining the stress-strain properties of paper with a solids content in the range 13-90% at constant strain rate. The tester was used to study

the influence of dry content, fibre swelling, beating, fibre length and fines content and furnish on breaking load. An overall picture of strength development was suggested: this involved interfibre friction, surface tension and formation of interfibre bonds at different moisture contents.

Ranger & Hopkins (61) critically analysed evidence in favour of interfibre bond failure, as opposed to fibre failure, and made an attempt to describe the tensile behaviour of paper on the basis of the predominance of fibre failure. The proposed mechanism of bond failure during plastic straining also serves to explain the phenomenon of strain lines.

A creep-measuring apparatus and a study of the viscoelasticity, creep and creep recovery of paper, covering the influence of fibre length, beating, wet pressing, drying under tension and moisture have been described by van Royen (62). A working hypothesis to explain creep and creep recovery is suggested, but the author concludes that some ten parameters, all dependent on manufacturing variables and fibre composition, would be needed for a complete mathematical description of paper behaviour.

The structure of paper has been analysed by Kallmes & Corte (63), structure being defined as the geometric arrangement of the fibres and interfibre spaces or pores. Paper was conceived of as consisting of a pile of thin layers, i.e. two-dimensional sheets of which the geometric elements are plainly visible. The structure of these sheets is described in terms of the means and distributions of eight geometric properties, which are closely related to the mechanical, optical and porous properties of paper. The equations are derived from probability theory and can be evaluated in terms of the number of fibres in a sheet and their dimensions. The equations were verified experimentally.

The rôle of polysaccharide additives in interfibre bonding was studied (64) by the absorption and retention at different dosage levels of a variety of starches and starch derivatives, compared with a high-viscosity polyvinyl alcohol and a polyethylene glycol. The influence of pretreatment of the pulp with guar gum was also determined. Burst and tensile strength and elongations values served as criteria of effectiveness of the additives. Different starches had different degrees of retention. The gains in sheet strength did not always parallel the amount of starch retained, but both retention and strength improvement were influenced by gum pretreatment. The study produced interesting evidence regarding the influence of additive structure and molecular weight on sorption and retention.

The effect on paper wet strength of various oxidised starches added at the wet end has been studied by Meller (65a), who ascribed their wet-strengthening effect mainly to carbonyl functional groups. An increase of up to 10% in the quantity of oxy-

starch increased wet strength. Prolonged soaking of treated sheets slowly decreased wet strength and the carbonyl oxystarches appeared to be sensitive to both acid and alkaline solutions, and when degraded their beneficial effect on dry strength was impaired. Meller (65b) has also investigated the effect on paper wet strength of the oxidation of the carbohydrate polymers in an eucalyptus sulphate pulp.

Jones *et al.* (66) have examined a series of periodate-oxidised maize starches, ranging from 0.10 to 96% conversion to dialdehyde chain products, and a selected group of oxystarches from other grain starches, as beater adhesives, deflocculating agents and surface sizes. No improvement in uniformity of formation was secured with oxystarches and retention was low. When used as surface sizing agents, the oxystarches produced high dry and wet strength. Experiments to establish optimum conditions for the development of wet strength with dialdehyde starches dispersed in presence of sodium bisulphite, have been reported by Hofreiter *et al.* (67), who found that manner of dispersion of the starch, use of alum and pH governed the retention obtained, and achieved excellent wet strength and improved dry strength with 0.5–10% application of the additive. Dittmar & Stein (68) have reported retention values for potato, maize and rice starches and discussed the retention mechanism and possible influence of the amylose and amylopectin components.

A sorption study has been made (69) with a partially methylated locust bean gum, in which gum retentions were determined directly by a radiochemical tagging technique. Experiments were carried out to determine the effect on rate of sorption of the variations in time, gum concentration, temperature, degree of agitation and pulp specific surface area. In general, both rate and amount of sorption are direct functions of specific surface. The major rate-controlling factor is a diffusional transport step bringing the gum molecules from the bulk phase of the solution to the surface of the fibres.

Despite the importance of the problem, data available on the influence of the moisture content on the properties of paper and board are far from complete. New testing equipment to measure the rate of dimensional changes in paper strips at controlled humidity and temperature has been described by Brecht & Hildenbrand (70), together with a systematic study to clarify the influence of furnish, beating, fibre orientation, drying and dried in strains on moisture expansion. This was found to depend much more on beating than on furnish, groundwood excepted. Fibre orientation and dried-in strains were also important. Furnish becomes important, however, if dimensional stability is desired together with, e.g., tensile strength, when hard pulps, which require less beating for strength development, are superior to soft pulps. High lignin

content slows down moisture expansion, and tension during drying can reduce moisture expansion considerably or, in extreme cases, even produce shrinkage on damping. The significance of the results is discussed with particular reference to the evaluation of the dimensional stability of printing papers.

Brecht (71) has also discussed the moisture sorption and desorption behaviour of paper and given graphs showing the moisture content at varying relative humidity levels for a number of pulps and papers. A survey is made of the influence of the moisture content on the strength properties of paper, degree of sizing, smoothness, especially after calendering and storage, the electrical properties, tendency to dusting, dimensional stability, blistering and curl.

Methods investigated for imparting dimensional stability to cellulosic products such as paper include catalysed heat treatment, formaldehyde cross-linking (72) and cyanoethylation (73). The last process is also reported to produce improved resistance to ageing, rot and acid; heat resistance is increased and dielectric strength and tensile strength retention are prolonged (74).

Finally, reference must be made to a valuable comparative study of stiffness testers (75a) and the development of a method for the quantitative evaluation of the 'handle' of paper. Brecht & Müller (75b) have carried out an extensive series of tests in which subjective evaluation of 'handle' was correlated with thickness, bulk, smoothness, hardness, elastic and superelastic rigidity and breaking load measurements on a large number of papers. The expression (bending rigidity)<sup>2</sup>/thickness was found to give optimum correlation, especially with a bending angle of 30° (Schlenker tester). The study also covered the influence on handle of basis weight and sheet density as affected, e.g., by wet pressing and calendering, fillers, furnish, beating and sizing.

An important conference on statistics and its application in the pulp and paper industry was held in Helsinki in May 1960, but the Proceedings have not yet been published, although several papers have already appeared in the periodical literature (76).

### Auxiliaries and specialties

In the field of auxiliaries, the work on wet strength resins and starch products has already been mentioned. Reference should, however, be made to a paper (77) on 'active aluminium hydroxide', which appears to improve both the dry and wet strength of hand-sheets made from unbeaten or partly beaten pulp. The active hydroxide can be precipitated on to the fibre or can be preformed and then added to the pulp. Dry-strength improvements do not surpass those obtained by beating, but sheets loaded with clay can be made which, by adjusting filler quantity, have improved

strength at the same opacity or improved opacity at the same strength.

A considerable advance has been made in the synthetic paper field with the development of fibrillating acrylic, polystyrene and other synthetic fibres described by Arledter (78). This development permits the use of conventional papermaking techniques for synthetic fibre flocs; heat- and pressure-bonding are, however, essential to develop the full strength properties of the sheet, although for, e.g., absorbent papers this heat-pressure-bonding step need not be carried to conclusion. Another advantage of the new fibres is that fillers, sizing agents, colours and other wet end additives can be employed in the normal manner. Numerous examples demonstrate the characteristics of the new materials obtainable.

The results of development work with Dynel and Fiber-B fibres have been reported by Brissette & Eldred (79). Although it is possible to bond dry 100% Dynel sheets, by passing through a calender heated to 300°F and with a nip pressure of several hundred lb. per linear inch, use of propylene carbonate solvent gives good bonding at reasonable temperatures and pressure. Fiber-B sheets can be bonded by damping the sheet to 20-30% moisture content and running the wet sheet over drying cylinders. Blending with cellulosic fibres facilitates machine operation. Some Dynel fibres have outstanding wicking properties, advantageous for filter papers, and papers from 75% Dynel are claimed to be self-extinguishing. Bonding in polythene coating can be improved by incorporating as little as 2-10% of Fiber-B (on weight of paper).

A readily dispersible new rayon fibre, RD-101, which can be formed into a web on a modified Fourdrinier machine, a cylinder machine or Kotoformers, has been described (80). Fibres with low or high bonding strength are offered, the lower bonding types giving soft, opaque sheets, while other types give strong, crisp, scuff-resistant sheets. Zinc chloride after-treatment gives an exceptionally strong and stiff sheet.

A most interesting summary of data obtained on the inter-relationship of the physical properties of synthetic fibre papers with (1) the mechanical variables of fibre length and diameter and sheet basis weight, and (2) the physical properties of the fibres, has been presented by Hentschel (81). Tensile strength increases with fibre length, reaching a maximum characteristic of the fibre used. The length at which the maximum is reached is directly dependent on fibre diameter. Tear strength increased essentially linearly as length increased, the highest level of tear strength being associated with the largest fibre diameter. Tensile and tear strength also rose to a constant level as the basis weight of the sheet was increased; again the basis weight at which maximum strength is reached is dependent on fibre diameter. Paper tensile strength was shown to



be linearly related to fibre tensile strength and paper elongation at break was linearly related to fibre elongation at break.

A new inorganic fibre, fibrous potassium titanate, has been described (82). An aqueous dispersion can be formed into sheets by pressure or vacuum filtration. The material is promising as filter medium, gasket material and for thermal, acoustic and electrical insulation. It blocks infra-red radiation, so providing an effective radiation shield. Thermal insulation is obtained at temperatures up to 2200°F.

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## PROTEIN FIBRES

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FROM the literature of the period under review, one theme appears to be reiterated: that protein fibres possess some parts which are crystalline and others which are amorphous. At first sight this seems like a mere restatement of the old 'micelle' theory; but whereas the old view regarded the differentiation as being largely fortuitous, it is now clearly seen to arise directly from localised differences in amino-acid composition and structure. The period has also coincided with two important events: the Second International Wool Textile Research Conference, and the Jubilee Conference of the Textile Institute, both held in May 1960. At the latter, Professors J. B. Speakman and W. T. Astbury gave useful resumé's. The writer, from his experience with regenerated proteins, believes that protein fibres are composed of corpuscular centres, the so-called amorphous regions being held together by sections of orientated and parallelised polypeptide chains, and it is interesting to find Prof. Astbury conceding that 'the more we see now of biological fibres, especially in the electron microscope, the more often they appear to have a corpuscular or string of beads basis, at least at some stage of their genesis'.

### Protein structure

The recognition of the  $\alpha$ -helix as a salient feature of protein structure was a noteworthy advance which prompted its extension towards the concept of the 'coiled coil' in keratin (1), but the idea is now in recession; it seemed at first to offer some hope of a structure in accord with X-ray diffraction results, but the equatorial reflection at  $27\text{\AA}$ , which Pauling and Corey considered crystallographic, has now been accounted for by the accepted micro-fibrillar structure, of which X-ray meridional reflections indicate a probable periodicity of  $25\text{\AA}$  (2). Also the A  $B_4$  cable is irreconcilable with a reversible  $\alpha$ - $\beta$  transformation, because the straightening of the polypeptide chains would still leave them twisted round each other. Skerthly & Woods (3) have found the existence of an intermediate state which is not sufficiently well-ordered to contribute to either the  $10\text{\AA}$  or  $4.65\text{\AA}$  equatorial peaks of



the transformation. The possibility of packing coiled helices without their forming twisted cables is also pointed out.

In connexion with the elastic properties of various kinds of silk, it has been demonstrated (4) by a series of amino-acid analyses that the more easily extended disordered regions of fibroin are rich in the amino-acids with long side-chains, while the well-oriented polypeptide chains in the crystalline regions consist of alternating residues of glycine and alanine or serine. These ideas have been extended to keratin (5), and it is suggested that short side-chains may preponderate in the crystalline regions of the protein. Skerthly (6) has found that finishing treatments of the urea-reducer type, which impart permanent set, do not appear to influence markedly the stability of the crystalline helical component in the keratin complex, while Andreeva (7) divides known protein configurations into two groups: those insensitive to amino-acid sequence, and those determined specifically by the arrangement of the amino-acid residues. A clue to the amino-acid sequence in the crystalline portions of keratin is suggested by Onions *et al.* (8), who observed differences in intensities of X-ray reflections at 198Å associated with the natural  $\alpha$ -structures. There has been a resurgence of interest in the cross  $\beta$ -structure (9), but the general conclusion is that no completely satisfactory molecular model has as yet been produced.

### Analytical techniques

There continues to be a widely felt concern about the sulphur balance of wool (10). Thus Maclaren *et al.* (11) are dissatisfied with present methods for estimating disulphide and sulphydryl groups in insoluble proteins; they believe that errors arise, especially during the preliminary hydrolysis, and they therefore devise new non-hydrolytic methods. A new analytical method for determining the extent of reduction in wool has been developed by Schoberl (12) and a quick and smooth reaction between sulphydryl groups and vinyl sulphones has been standardised by model experiments with cystine. Lane and his colleagues (13) have found seven  $^{35}\text{S}$ -labelled compounds in addition to  $^{35}\text{S}$ -cystine and  $^{35}\text{S}$ -methionine in acid hydrolysates of wool. From a similar study of  $^{35}\text{S}$ -labelled oxidised wool the authors conclude that the cystine in wool cannot be accurately determined as cysteic acid after oxidation of the wool with peracetic acid.

The tryptic hydrolysis of  $\alpha$ -keratose (14) has allowed the isolation of the free amino-acids arginine and lysine, eight dipeptides of either arginine or lysine, two tripeptides, a pentapeptide and possibly a hexapeptide. Bradbury (15) has isolated a sample of cuticle-rich material which contained 27% more proline and 40% less dibasic acids than the parent wool.

### Wool

The efficiency of dieldrin has again been proved both in the field, for control of blowfly strike (16), and in the dye-house as a permanent mothproofing agent (17), where its protective efficiency exceeded 94%. Another biological factor is bacterial discoloration, concerning which Fraser & Truter (18) conclude that the defect will occur only if the fleece contains adventitious bacterial nutrients which arise through damage to the hypersensitive skins of susceptible sheep.

### Fine structure

An explanation for the mechanical properties of keratin has generally been sought in terms of molecular structure but some authors believe that the details of load-extension curves arise from the nature of the microfibrillar-matrix units. Alternative X and Y zones along microfibrils are proposed. The former are crystalline, but the latter are regarded as being heavily cross-linked possibly to themselves and their surrounding matrix; their bulky side-chains also supply a measure of steric hindrance (19). Another suggested model is based on the view that the contractile structures of the fibre are not cross-linked by disulphide bonds, but are embedded in material containing inter- and intra-molecular disulphide bonds (the matrix), the rate of plastic deformation of the latter being affected by sulphydryl interchange (20). The bilateral nature of the wool cortex continues to be a focus of interest (21). Satlow (22) contends that differences in the reactivity or number of disulphide bonds may account for asymmetry; he has perfected a rapid and simple method of detection. On the other hand it is suggested (23) that the phenomenon may be due to differences in accessibility, rather than to quantitative chemical differences. The solubility of the two bilateral fractions has been studied (24). The ortho-cortex is the most readily dissolved and is thought to contain intra-chain disulphide linkages. Electron-microscopical studies of the cuticle before and after the deposition of metal sulphides have revealed the distribution of chemically active groups and provided pictures showing a marked degree of contrast (25). Staining and microscopical studies of coarser wools have demonstrated the presence of a core that is more basophilic than the ortho-cortex, and which it is proposed to call the meta-cortex; the meta-cortical cells appear to be deficient in sulphur (26).

### Chemical properties

There was a time when chemists and physicists were at loggerheads about the combination of acids with keratin; the former had demonstrated the quantitative basic reactivity of amino groups, whereas the latter had denied the possibility of large molecules

penetrating the crystalline structure of well-ordered polypeptide chains. It has now been found that the units of fibrous proteins are more extensive than was originally realised and both chemists and physicists are now reconciled to the idea of ordered zones with short inert side-chains, connected to amorphous regions comprising polar-groups. These latter may be either acidic or basic, and the quantitative prediction of their behaviour has been accurately described either by the Gilbert & Rideal theory, or by the Donnan equilibrium. The former has recently been further elaborated (27), and titration curves have been plotted for acids absorbed by wool from solutions containing organic solvents (28); the diffusion of sulphonic acids into keratin in the presence of water and alcohol has also been studied (29). Carbonisation has been found to cause a specific increase in the number of serine and threonine end groups (30). Neutralisation of the stoved wool up to pH 8.6 effects a recovery of serine and threonine peptide bonds, and the complete neutralisation of carbonised wool is recommended.

Keratin may be solubilised either by reduction or oxidation (31) but despite the disruption of disulphide bonds in many different ways, there is no conclusive evidence that a reproducible and homogeneous protein component has been isolated (32). Sedimentation and light-scattering studies on soluble fractions have shown that their aqueous solutions are polydisperse with varying molecular weights and polarities. Thompson & O'Donnell (33) believe that performic acid is preferable to peracetic acid for oxidative solubilisation.

Considerable interest has lately centred on the yellowing of wool following heating, irradiation, oxidation and other causes. When fibres were sulphonated, treated with aluminium sulphate, or a mixture of borax and boric acid, or of T.H.P.C. and urea (34), they were less susceptible to yellowing at 200°. It is believed that yellowing is due to cystine breakdown, but an intense discoloration may involve tyrosine residues (35). The measurement of yellowing has also been considered (36), and the damage found to increase with pH. Earland *et al.* (37) have found that many proteins become coloured by oxidation, and that this process shows similarities with that caused by irradiation. Wool damage has been further assessed by use of an alkaline thioglycollate extraction technique (38), which has been compared with the alkali solubility method.

Wool has been modified chemically by cyanoethylation, benzylation and formalisation under tension (39), while the sulphydryl groups in reduced fibres have been reacted with bifunctional divinyl sulphones, dimethyl maleate, *N*-*p*-phenetilmaleinimide to give stable thio-ether bonds (40). There is thought to be a direct correlation between the sulphydryl content of wool and the formation of lanthionine (41); this latter is assumed to follow from a side-reaction occurring simultaneously with disulphide exchange cross-

linking. The reactivity of *N*-mercaptomethyl-poly-hexamethylene-adipamide disulphide has been compared with that of keratin (42); it has been demonstrated that the failure of oxidised wool to undergo exchange reactions is not inconsistent with the fibres containing sulphonic acid groups.

### Dyeing

The use of reactive dyes continues to be investigated. For example, the fastness properties of Procion dyes have been considered in relation to the practical dyeing of wool and wool/cellulose unions, and the application of the dyes from dyebaths containing solvents (43, 44). By applying an indicator-dye it has been shown that an increased acid-dyeing rate can be obtained in the presence of alcohols, while an increased basic-dyeing rate could only be obtained with the assistance of organic amines. Dyeing rates have also been studied in relation to surface properties, and the causes of some variations have been elucidated (45). It has been claimed that brighter shades may be obtained at sub-boiling temperatures (46), because the yellowing of the fibres is then avoided. Harrap (47) has been able to dye wool in 1–2 minutes, at room temperature, by substituting 85% of anhydrous formic acid for the water which is normally the basis of a dyebath.

### Shrinking and felting

Wool fibres have been chemically modified in many different ways in order to reduce their felting shrinkage, and a comprehensive survey of this field has been made by Nitschke (48). The writer feels that the best procedure is to impregnate the fibres with a diacyl chloride, and then to immerse them, at room temperature, in an aqueous solution of an appropriate  $\omega$ -diamine. The reaction is very rapid, the reagents readily available, and a polyamide is deposited in the macro-pores of the wool. Because polyamides are structurally related to proteins, the handle of the material remains soft and attractive. This process shows similarities with that with thiazolid-2,5-dione, where polyglycine is formed in the fibres (49). It is claimed that 'spot-welding' is unlikely to be an important feature in the process (50). The efficiency of shrink-proofing is said to be matched by the severity of surface modification observed by microscopy (51), and this applies to all treatments in which there is little or no attack on the whole fibre. Regarding the physical properties of felts, a comprehensive tensile strength, density and modulus index has been proposed for the measurement of felt quality (52).

### Wool scouring

Experiments designed to compare the processing of solvent-degreased wool with that obtained by soap-soda scouring have

been described (53). It has been shown that card and comb production rates considerably higher than normal are possible with solvent-degreased wool, and that a higher combing tear and a better top can be produced. Nitschke (54) recommends that scoured wool should retain not less than 0.5% wool grease, since this has a beneficial effect due to hygroscopicity. The quantitative, chromatographic analysis of suint extracts from raw wool has shown the presence of volatile acids, higher fatty acids, dicarboxylic acids, hydroxy- and keto-acids, aldehydes, sugar acids, phosphorylated sugars, polypeptide material and urea (55). Many advantages over conventional methods are claimed for a process in which raw wool is cleaned by anaerobic fermentation (56).

### Silk

Glycine with isotopic carbon in the  $C_{(1)}$  position has been injected into silkworms, and the fate of the amino-acid followed by tracer techniques (57). The direct conversion of glycine to serine and also to alanine was thus demonstrated, the labelled carbon remaining in the  $C_{(1)}$  position. With the same technique it has been shown that formate carbon is used by the organism *Bombyx mori* for the synthesis of glycine, where the labelled carbon goes into both  $C_{(1)}$  and  $C_{(2)}$  positions (58). The biosynthesis of silk fibroin with isotopic carbon has also been studied in Japan (59), where the conversion of glyoxylic acid to glycine has been traced. When alanine  $^{14}C_{(1)}$  and glycine- $^{14}C_{(1)}$  were injected for synthesis *in vivo*, the N-terminal amino-acids showed a radioactivity seven times that of the non-terminal acids (60). By a radiochemical technique, fibroin synthesis by ribonucleic acid metabolism in the silk gland was indicated (61). The light resistance of silk fibroin is said to be greatly improved by methylation with diazomethane (62), while irradiation with  $\gamma$ -rays *in vacuo* is claimed to improve dynamometric properties (63) and to increase the viscosity of fibres dissolved in cuprammonium solution.

### Regenerated protein fibres

Large enterprises retain a certain momentum, and when in 1957 the commercial production of 'Vicara' and 'Ardil' ceased, there was for a time a continued publication of work previously in hand. During the period under review there has been a marked diminution in the quantity of such literature references, although further researches on the denaturation of groundnut proteins have been reported (64). Fibres from milk-casein were first in the field and still stay the course. Courtaulds Ltd. produce 'Fibrolane' for both carpets and felts, and the physical properties of the fibres have been improved with the appearance of 'Fibrolane XL'. Resorcinol has again been used for cross-linking, and Genin (65) finds that it is

best to use a formaldehyde/phenol ratio of more than 12 : 1. The author has fractionated milk-casein into  $\alpha$  and  $\beta$  forms, the  $\beta$  variety giving the stronger fibres. The use of heavy metal salts as tanning agents continues to be studied and a modification of chrome-tanning has been protected (66). Specific types of zirconium salts, which have the great advantage of being colourless, are also being investigated (67).

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## SYNTHETIC FIBRES

### POLYAMIDES (R. F. Moore, M.A., B.Sc., D.Phil.)

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RECORD production of polyamide fibres for 1960 and plans for worldwide expansion in the future are due partly to the increasing end-uses for the fibres and to the encroachment of nylon into the tyre cord field. No serious contenders to 6.6- and 6-nylon have appeared; new routes through cyclohexane and toluene to caprolactam, the monomer for 6-nylon, make it potentially cheaper than 6.6, with which it is at present comparable as regards price.

The total production of polyamide fibres for 1960 in the U.S.A. is estimated at 320-375 million lb. (including 150 million lb. tyre cord yarn); by 1965 it is expected to reach 550-670 million lb./annum (1, 2). Du Pont are increasing considerably their capacity for 6.6 tyre cord (1), and for carpet yarn (3). Of the 6-nylon producers, Allied Chemical Corp. plan to triple production of tyre cord (4) and to become the first American company to make and sell 6-nylon apparel fibre in the U.S. (2, 5), whilst American Enka (6) and Dow Chemical Corp. (7) are also to contribute to the increase in production of heavy denier yarns. In the U.K., production of 6.6-nylon continues at record levels (8). Imperial Chemical Industries Ltd. are planning the manufacture of 15,000 tons/annum of caprolactam for 6-nylon, not hitherto produced in Britain (9). Competition in the 6-nylon fibre field may also be supplied shortly by British Enka (10), while many countries plan to initiate or expand production.

Several new polyamide fibres have recently become of interest commercially. A Russian fibre, 'Perlargon', is a 9-nylon, produced from  $\omega$ -aminopelargonic acid. It has a lower melting point and moisture absorption than 6- or 6.6-nylon, with tenacity 7 g./denier and elongation 18% (11). In Japan trial production has commenced of 'U-rylon', made by polycondensation of nonamethylenediamine and urea (12). Du Pont are now testing a tyre cord yarn, of unpublished constitution, with melting point about 315° as compared with the normal 250° (13). The same company have also developed a new elastic fibre, 'Lycra', containing at least 85% of segmented polyurethane, which has lighter weight and greater retaining power, flex life and durability than rubber (14).

*Finishing and texturing*

The finishing or texturing of nylon yarns for specialised end-uses continues to develop along two lines, firstly the spinning of yarns with non-circular cross-section (15), and secondly the imparting of deformations to the yarn (crimps, curls or loops), or a combination of both processes. Fabrics made from du Pont's 'Antron' (16), having a tri-lobal cross-section, are claimed to have a distinctive dry 'hand' and improved print definition and clarity. Texturing processes for nylon yarns have been summarised (17). Their application to mixtures of fibres enables yarns to be obtained comprising a nylon core encased in a sheath of another fibre (18). The properties of nylon yarns can be improved by the radiation-induced grafting of vinyl polymers on to the fibres. Thus the grafting of methacrylic acid to 6.6-nylon lowers its electrical resistance and decreases its solubility (19), whilst with *N*-vinylpyrrolidone, improved dyeability, increased moisture retention and reduced static charge are claimed (20). Similar treatment with sodium styrenesulphonate is also purported to improve the static properties (21). An improved process has been described for the coloration of nylon by melt-spinning polymer chip coated with a finely divided dispersion of polyamide and pigment (22). Various additives have been claimed to improve the stability of polyamides. Heat stabilisers disclosed include esters or amides of phosphorus oxy-acids (23a), copper halides (23b) and iodobenzoic acid (23c). Manganese phosphate is claimed to improve the light stability of delustred polyamides (24).

*Polymerisation technique*

Improvements in polymerisation procedures have been concerned mainly with effecting the reaction at lower temperatures, e.g., by using inert diluents such as phenols (25a) or hydrocarbons (25b), continuously and at atmospheric pressure (26). In one example, a low-viscosity pre-condensate is allowed to flow down narrow, vertical steel wires at high temperature, under nitrogen, to complete the polymerisation (27). Isocyanates, carbodi-imides and cyanamides have been disclosed as accelerators for the polymerisation of lactams (28) and *N*-acetylcaprolactam (29a) and alkylamine hydrochlorides (29b) have been used as viscosity stabilisers.

The technique of polymerisation by interfacial poly-condensation has received considerable attention (30) and been used to prepare a number of the novel polyamides disclosed. These include polymers containing phosphorus (31), sulphur (32) and silicon (33) combined in the chain. Piperazines have been investigated further as the diamine constituent in polyamides (34). Copolymerisation of 4-aminomethylcyclohexanecarboxylic acid with caprolactam raises

the melting point of the final polymer (35), whilst oxalic or *trans*-1,4-cyclohexanedicarboxylic acid (36a) and 1,4-bis(aminomethyl)-cyclohexane (36b) have the same effect on polyamides derived from *m*-xylylenediamine. An improved process for making these has been described (37). Much attention has been paid to polymers containing urethane links. These play an important part in the new yarns with built-in elasticity (cf. 'Lycra', mentioned above), and are composed, for example, of chains of polyether segments joined via urethane links to a polyamide, polyurethane or polyurea segment (38). The resultant linear copolymers have repeating segments of alternate high and low melting point and can be melt-, wet- or dry-spun to give fibres remarkable for their high elastic recovery (>90%) and low stress decay (<20%). Similar elastic polymers containing hydrazide links have been described (39).

The research results in the field of new polyamide fibres have been reviewed (40).

Amongst the more practical of the many contributions to the physical aspects of polyamide chemistry are further investigations into the kinetics of the water-initiated polymerisation of caprolactam (41). Miyake has characterised a large number of nylons using infra-red and X-ray techniques and found almost complete hydrogen bonding, irrespective of the number of methylene groups (42). The effect of spherulites on improving the mechanical properties of 6.6-nylon has been studied further (43), whilst considerable attention has been paid to the effect of moisture on the dynamic mechanical properties of polyamides (44), which is of interest in connexion with the flexing of tyre cords. Thus the loss peak and modulus dispersion at 97° in dry 6.6-nylon is shifted to lower temperatures with increasing water content (44b). Nuclear magnetic resonance has also been used to study the effect of moisture on segmental motion in polyamides (45).

### Intermediates

Many recent patents dealing with the manufacture of 6.6-nylon intermediates are concerned with improvements of established processes. Few of the alternative routes studied are likely to be of immediate commercial importance. The reductive hydrolysis of aniline to either KA (cyclohexanol/cyclohexanone) (46a) or the ketone alone (46b) has received further attention, and cyclohexanone has also been obtained by the autoxidation of cyclohexylbenzene (47). Hexamethylenediamine has been produced by the hydrogenation of caprolactam methyl ether (48a) and 5-amino-methyl-2-furfurylamine (prepared from sugars) (48b).

Several routes to 6-nylon intermediates which are of potential commercial interest have been investigated, including the oxidation of cyclohexylamine to cyclohexanoneoxime in almost quantitative

yield by hydrogen peroxide in the presence of tungstate catalysts (49). The oxime has also been prepared from nitrocyclohexane by reduction with hydrogen and lead catalysts (50a), and with carbon monoxide and alcohols (50b). A possibly very important discovery is disclosed in recent patent applications by Snia Viscosa in connexion with the nitrosation of cyclohexyl derivatives (51, 52). With cyclohexanecarboxylic acid and nitrosylsulphuric acid in oleum, nitrosation, decarboxylation and rearrangement to caprolactam can be accomplished in one stage in better than 80% yield. This opens up a new and potentially cheap route from toluene  $\rightarrow$  benzoic acid  $\rightarrow$  cyclohexanecarboxylic acid  $\rightarrow$  caprolactam.

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## ISOTACTIC POLYPROPYLENE FIBRES

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THE discovery of the stereospecific polymerisation of  $\alpha$ -olefins has resulted in a new range of potentially cheap fibre-forming polymers (*1*). Large-scale activities are based predominantly on fibres from polypropylene and the two applications of this material (plastics and fibres) have widened the activities of primarily chemical or textile organisations.

In the early part of 1959 a new synthetic fibre of high quality and low production cost (2) was produced by the Polymer Company, a Montecatini subsidiary, and was said to be usable alone, or in admixture with other fibres. Commercial production was due to start by the end of the year. This fibre has been named 'Meraklon', as distinct from the polypropylene for plastics applications ('Moplen'). By May 1960 the Polymer Company's plant at Terni was reported to be producing yarn at 3,000,000 kg. per annum and by 1961 a production of 100 tons daily (3) is expected.

Imperial Chemical Industries Ltd. have obtained an exclusive licence from Montecatini for the production of polypropylene staple fibres, filaments yarns and monofilaments in the U.K. (4), in addition to the production of the polymer for use as a plastic. In 1959 British Celanese, now a Courtaulds subsidiary, were reported to be producing trial quantities of fibre from polymer produced by Shell (5) called 'Courlene PP'. This material, although dearer than the polyethylene fibre 'Courlene X3', was said to be more resilient and to have a 5% higher yield (lower density) (5).

Elsewhere in Europe, interest in the production of polypropylene-based fibres is reported—in Austria (6), France (7), and Germany (8).

In the U.S.A. wide interest is being shown in fibres from polypropylene, where Montecatini are marketing 'Meraklon' (9). Several U.S. manufacturers are engaged in developing products of their own (10-17). In Canada, Canadian Celanese are producing a polypropylene fibre under the trade name 'Propylon' (18), and Courtaulds Plastics, Canada Ltd. have been appointed as distributors, in that country, of Avisun's products (19). Japanese chemical and textile concerns also have polypropylene development programmes, based on a tie-up with Montecatini (20), or with American interests (21), or on an allegedly patent-free polymerisation route developed in Japan (22). Interest in polypropylene fibres has also been shown in Israel, where production will start at the Ashdod factory of Rogasin Industries in 1961 (23).

The outlets envisaged for polypropylene fibres cover a wide range of industrial and domestic uses, and require the production of staple fibre, continuous filament yarns, and thick monofilaments. In most cases the first development outlets have been into the rope (24) and cordage field, where the properties of the fibre are shown to great advantage. There have been reports of favourable reception of heavy duty marine hawsers made of polypropylene for use in various marine and industrial fields (25). Other industrial outlets include non-woven netting (26), webbing and car seat covers (27), tarpaulins and tents (28) and covers for battery electrodes (29).

One of the first non-industrial applications of polypropylene fibres was in carpets, though trials are being made to widen the

scope into the textile field, etc. (31). It is claimed that success has been obtained with blankets, light suitings and men's socks, used alone or blended with other fibres. Polypropylene is said to blend well with wool (30). The emphasis placed on the various outlets by a major Japanese firm is discussed (31).

### *Properties*

The initial development of polypropylene fibres for industrial end uses, and in particular ropes, cords and other marine outlets, reflects the properties of the fibre. Its low density ( $\sim 0.90$ ) enables it to float on water and also provides a high yield. It has high strength, good elasticity and abrasion properties and the cheapness of the monomer should facilitate its competition against the natural fibres. Other advantages are its insensitivity to moisture and its good resistance to solvents and chemical attack, although an exception to the latter is the relative sensitivity to oxidation, which demands the use of stabilisers (32, 52). Other disadvantages such as low melting point and dyeing difficulty would not be expected to be major drawbacks in the marine ropes and cordage field. The development and properties of polypropylene fibres are reviewed (33), the 'steric purity' being reported as an important factor governing the elastic properties; elsewhere, the fractions of the polymer soluble in ether and heptane are stated to have a 'plasticising' action on the fibre (34). Other reviews summarise the development, production, properties and applications of polypropylene fibre (35, 36).

### *Production technique*

Although a number of patents (37, 38) have described processes for producing polypropylene fibres by wet- and dry-spinning techniques, the bulk of the evidence shows that production is based essentially on what can by now be regarded as a more or less conventional melt spinning and drawing route. The use of a screw extruder of special design for melt spinning polypropylene fibres alone, or to supply molten polymer under pressure to a metering pump, is described (39). The use of steam (40) and hot conditioning systems around the threadline (41) are also claimed in the patent literature; the use of high spinning temperatures (more than  $100^{\circ}$  above the melting point) (39, 42, 43) and of prefiltration (44) are also reported. The rôle of the molecular orientation introduced during spinning is emphasised in two patent specifications (45). The use of 'plasticised melt spinning' (46), which presumably avoids the need for high temperatures, and a process for controlled cooling of the molten threadline, is of considerable interest (47). The formation of polypropylene fibres by melt extrusion is discussed in a paper by Russian workers (48), where again the benefits of plasticised melt-spinning are described.



Several sources discuss the improvement in the properties of polypropylene fibres by an additional drawing or heat treatment. Yarns of improved dimensional stability (49) and enhanced elastic properties (50) and a drawn product with very low shrinkage (3½% at 250°F) (51) have been obtained; Russian workers publish the results of an investigation of a second drawing and/or relaxation treatment (52). The orientation of isotactic polypropylene filaments has been studied by means of X-rays (53).

As has been mentioned earlier, one of the defects of isotactic polypropylene, as a fibre-forming material, is its susceptibility to thermal oxidation (54). The use of antioxidants which can survive the drastic thermal conditions used in melt-spinning is described (55-58). As might be expected, the same compounds should be at least partially effective for polypropylene, polyethylene and polyvinyl chloride (59).

Polypropylene fibres are also susceptible to attack by ultra-violet radiation, and if they are to be acceptable in the industrial and domestic textile markets, it is necessary to include additives to minimise light tendering (55, 56), coupled with antioxidants to improve the weathering properties (60). The interest in this problem is reflected by the range of ultra-violet absorbers now available commercially, and particularly by the announcements of new compounds (61).

As with other synthetic fibres, polypropylene fibre suffers from the fact that it is difficult to dye by normal commercial processes and a great deal of effort is being deployed with much success to remedy this defect (62). Techniques for incorporating carbon black (63) and other pigments (64) into polypropylene are of interest to fibres and plastics manufacturers. The problem of improving the dyeability has been tackled in many ways, including the use of dyes soluble in polypropylene, making use of non-aqueous dyebaths, etc. (65), the grafting of a second (dyeable) polymer on to the surface of the fibre (66), the blending of the polymer with a dyeable additive prior to spinning (67) and the chemical treatment of the fibre, either before or after drawing (68). Sometimes two such modifications are shown to be advantageous, e.g., blending with an additive prior to spinning, followed by a further chemical after treatment of the yarn (69).

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### POLYESTER FIBRES (N. D. Scott, B.Sc., Ph.D.)

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WORLD consumption of polyester fibres has continued to expand during 1960 to such an extent that there has been some shortage of the intermediate, dimethyl terephthalate. There have been numerous reports of increased capacity for making intermediates and polymer and fibre by many companies in different parts of the world (1-19).

These reports include details of the production technology of the Russian polyester fibre 'Lavsan' (19a) and a review of Russian achievements in the field of polyester and other synthetic fibres (19b).

There is a growing interest in improving the fabric properties of polyester fibres by using fibres of non-circular cross-section (20). A new type of filament yarn called 'Dacron 62' having a tri-lobal cross-section (21) has been introduced by du Pont. It is said to impart to fabrics improved handling, covering and dyeing properties (22).

#### *Intermediates for poly(ethylene terephthalate)*

Associated with their venture into polyester fibre manufacture, Russian research workers have published a number of papers on methods of preparing *p*-xylene and terephthalic acid (23).

Air oxidation of *p*-dialkylbenzenes continues to attract interest and patents have appeared dealing with catalytic oxidation in aliphatic acid solvents in the presence of bromide and peroxide-forming additives (24), bromide and chloride (25) or chloride alone (26). Methods of controlling the process (27), recovering bromine from the off-gases (28a) and improving yields and quality of the terephthalic acid produced have also been described (28b).

The use of a fluidised-bed technique has been disclosed for the preparation of terephthalic acid by the Henkel process (29a), or by air oxidation (29b) and for the preparation of esters of carboxylic acids (30). Other disclosed aspects of the Henkel reaction are concerned with the recovery of catalyst (31a) and the removal of reaction by-products (31b). A new process for making terephthalic acid from toluene by chloromethylation and oxidation has been developed in Germany and is claimed to give a product of improved purity (32). Two useful reviews of terephthalic acid processes have been published (33).

Several new methods of purification of the acid have been described and include recrystallisation of the crude acid from benzoic acid (34), *NN*-dimethylformamide (35), a dialkyl sulphoxide (36a), toluic acids (36b), water at high temperatures in non-ferrous equipment (36c) and from an *N*-alkylpyrrolidone (37), or sublimation of the crude acid from a fluidised bed (38). Chlorination in an organic solvent with gaseous chlorine has been used so that side-chain chlorination renders the *p*-toluic acid and its alkyl esters soluble in the solvent (39). Other purification processes involve conversion to an alkali metal salt of the mono- $\beta$ -hydroxyethyl ester (40) or air oxidation of the liquid dialkyl esters (41).

There has also been some interest in the separation of mixtures of terephthalic, isophthalic and other benzenecarboxylic acids as obtained from the oxidation of mixed xylenes (42).

Papers on the mechanism of the carboxylate rearrangement reaction (43) and the ester interchange equilibria between dimethyl terephthalate and ethylene glycol have been published (44).

#### *Preparation of poly(ethylene terephthalate)*

Continuous polymerisation systems have been described in a number of patents (45), although there is no indication of commercial exploitation of these. The direct esterification of terephthalic acid with ethylene glycol has also attracted some interest (46) and Japanese manufacturers are reported to be planning the large-scale use of this process (47).

In addition to the usual catalyst claims, process improvements are said to be derived from polymerisation in the presence of orthophosphoric acid or an alkali metal acid phosphate (48), or in the presence of carbon black (49a). A method of controlling polymerisation by introduction of a monofunctional substance (e.g.,

*o*-benzoylbenzoic acid) into the reaction has been disclosed (49b). Poly(ethylene terephthalate) can also be prepared by the polymerisation of the cyclic trimer, tetramer and pentamer of ethylene terephthalate (49c).

A detailed study of the kinetics of the polycondensation reaction (50) shows that it is second-order, with an activation energy of about 31 kcal./mole. In thin layers (1 mm. and under) the rate constant of the catalysed polycondensation reaction is inversely proportional to the thickness of the layer (51). The activation energy (11–14 kcal./mole) was considerably less than that found for bulk polymerisation (35 kcal./mole) and presumably improved heat transfer and easier evaporation of ethylene glycol facilitate the reaction.

#### *Properties of poly(ethylene terephthalate)*

More studies of the crystallisation and crystal structure have been reported. The relationship between temperature and degree of crystallisation (52), the effect of methyl ketones in inducing crystallisation (53) and the structure of polymer spherulites (54) have been commented upon and the action of various plasticisers described (55). The elastic modulus of the crystal unit has been calculated (56) and an X-ray diffraction method of determining crystallinity described (57). A review of methods of measuring crystallinity in poly(ethylene terephthalate) shows that for oriented fibres, infra-red spectra give high values, X-ray measurements low values, and density measurements intermediate values (58). Further detailed assignments of the infra-red spectra have been reported (59).

Molecular weight studies include three papers on end-group determinations (60) and two on fractionation systems (61).

The kinetics of the hydrolysis of poly(ethylene terephthalate) by water (62a) and by hydrochloric acid (62b) have been studied and the effects of nuclear radiation investigated (63). The technique of differential thermal analysis gives a new method of measuring transition phenomena in the polyester (64). The preparation of colloidal solutions of the polymer has been claimed by Russian workers (65).

Four distinct oligomers have been identified in poly(ethylene terephthalate) (66) and their structures elucidated. The effect on the properties of the substitution of chloro-, bromo- and methyl-groups on the benzene ring has also been studied (67).

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## PLASTICS

### By MEMBERS OF THE PLASTICS AND POLYMER GROUP

(Convenor: J. E. S. WHITNEY, B.Sc., F.R.I.C.)

#### INTRODUCTION (J. E. S. Whitney)

*Catalin Ltd.*

THE Rubber and Plastics Research Association of Great Britain was inaugurated on 15th November 1960 by the incorporation of a number of member-companies of the British Plastics Federation into the Research Association of British Rubber Manufacturers. The plastics interests of the Association will be represented by both a Plastics Research Committee and membership of the Council.

The boom experienced by the plastics industry in 1959 was arrested during the early months of 1960. The year was marked by a steady progress in the face of increasing world competition and a marked tightening in the demands from the home market by the imposition of credit restrictions. Overall sales of plastics material during 1960 have been estimated at approximately 550,000 tons, comprising 340,000 tons of thermoplastics and 210,000 tons of thermosetting materials (see Table I). Imports, however, increased by 70% on the 1959 figures, to 93,321 tons, while 171,173 tons of plastics materials were exported.

In the thermoplastics field, marked price reductions were effected in polyethylene and polyvinyl chloride. Despite an increase in the production of polyvinyl chloride by 20% to 105,000 tons, 28,000 tons of polymer and 7000 tons of compound were imported. A further increase in plant capacity of 25,000 tons is planned for 1961, which, it is anticipated, should help counteract the high level of importation. Indigenously produced polypropylene became available during the last quarter of 1960. 105,000 tons of low-density polymers and 40,000 tons of high-density polymers, mainly polyethylene, were produced. The overall production capacity for high- and low-density polyolefins is expected to increase to 200,000 tons during 1961.

The continued increase in demand for thermosetting materials was maintained during 1960, and sales of well-established materials such as phenolics and aminoplasts maintained a significant contribution towards this increase. It is estimated that the sales of



**Table I**  
*Sales of plastics material (tons) in 1960*  
*(Figures given by the Board of Trade)*

	Jan. to Mar.	April to June	July to Sept.	Oct. to Dec.
<i>Thermosetting materials</i>				
Alkyds:				
Solid and liquid resins .. .. .	10,219	10,995	9397	8841
Solutions, emulsions and dispersions (net resin content) .. .. .	2463	3285	2194	1934
Other .. .. .	141	149	148	141
Aminoplastics:				
Solid and liquid resins, including solutions (net resin content) .. .. .	8282	8392	7941	8031
Moulding and extrusion compounds .. .. .	7224	6829	6141	7098
Casein plastics:				
Sheet, rod, tube and profile shapes .. .. .	373	339	344	430
Phenolics and cresylics:				
Straight solid and liquid resins .. .. .	4446	4149	3934	4494
Modified solid and liquid resins .. .. .	1086	1078	841	857
Solutions, emulsions and dispersions (net resin content) .. .. .	1141	1254	1283	1381
Moulding and extrusion compounds .. .. .	8028	7542	7288	7712
Decorative laminated sheet .. .. .	2913	2315	2018	2407
Other laminated sheet .. .. .	2159	1911	1879	2178
Cast sheet and laminated or cast rod, tube and profile shapes .. .. .	1008	1005	907	1089
Polyesters .. .. .	2063	2307	1894	2097
Other thermosetting materials .. .. .	3284	3169	3086	3174
<i>Total thermosetting materials</i>	<i>54,830</i>	<i>54,719</i>	<i>49,275</i>	<i>51,864</i>
<i>Thermoplastics materials</i>				
Cellulose:				
Moulding and extrusion compounds .. .. .	1563	1565	1607	1547
Other (including photographic film base) .. .. .	1924	1713	1731	1876
Polyvinyl chloride:				
Solutions, emulsions and dispersions (net resin content) .. .. .	475	453	553	742
Moulding and extrusion compounds .. .. .	12,956	12,340	10,669	13,736
Plasticised sheet .. .. .	10,802	11,235	9577	11,525
Unplasticised sheet .. .. .	1058	905	798	877
Rod, tube and profile shapes .. .. .	1029	1499	1145	956
Polyethylene and polypropylene:				
Granules and moulding and extrusion compounds .. .. .	24,749	23,458	19,121	20,861
Sheet, rod, tube, film, foil and profile shapes .. .. .	4274	4651	4440	5101
Polystyrene:				
Moulding and extrusion compounds .. .. .	9371	9446	8450	9853
Other .. .. .	1623	1661	1420	1005
Polyvinyl acetate (net resin content) .. .. .	3908	3991	3321	3327
Other thermoplastic materials (including acrylics, polyamides, polytetrafluoroethylene and polyvinyl chloride resins (i.e., polymers sold as such) .. .. .	18,826	16,545	16,676	18,058
<i>Total thermoplastic materials</i>	<i>92,558</i>	<i>89,462</i>	<i>79,511</i>	<i>89,464</i>
<i>Total all plastics materials</i>	<i>147,388</i>	<i>144,181</i>	<i>128,786</i>	<i>141,328</i>

(Note. In years prior to 1960 error was made by the inclusion of about 400 tons under 'Other Thermoplastic Materials' instead of under 'Other Thermosetting Materials'.)

reinforced plastics increased from 11,000 tons in 1959 to 12,000 tons in 1960.

Considerable interest has developed during recent years in synthetic polymeric materials, based upon or containing combinations of skeletal elements other than carbon. Although research at this stage is mainly in the laboratory, it is anticipated that this field is one in which exciting new developments will arise. In consequence it is considered appropriate to include a review of current work in this plastics chapter.

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### METHACRYLATES (P. R. Cowley, Ph.D., and W. E. Frost, M.A.)

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METHACRYLATES were last reviewed in these Reports in 1955 (1), but the subject has been treated elsewhere more recently (2). The well-known sheet and moulding powders based on polymethyl methacrylate are still the most important group of products. Other forms of methacrylates, production of which is expanding, include solution polymers (oil additives and paints) and dispersion polymers (paper treatment, paint bases, textile applications). Production of methyl methacrylate monomer has increased considerably. The major producers all operate the established route from acetone through acetone cyanhydrin, but attempts have been made to discover cheaper syntheses; for example, from isobutene by oxidation to  $\alpha$ -hydroxyisobutyric acid and the dehydration of the latter or its esters to methacrylic derivatives (3). Other alkyl methacrylates are available commercially, but are only used on a relatively small scale.

The polymerisation of methyl methacrylate has been studied over a very wide temperature range—up to 180° (4a) and 225–300° (4b). Variations on the conventional peroxide and azo initiators have been examined and references to work on novel types of catalyst are listed in the bibliography. Even conventional free-radical initiators at low temperatures can give syndiotactic polymethyl methacrylate (cryst. m.p. 200°). Anionic initiators have been reported to give syndiotactic polymers in highly solvating media, an isotactic polymer in hydrocarbons, and an isotactic-syndiotactic block copolymer in media of moderate solvating power (5). In some cases solvent treatment is required to develop crystallinity. No mechanical properties have been published.

Further information is now available on some of the factors affecting the technical scale polymerisation of methyl methacrylate. It is reported that the discoloration of dyes which occurs in peroxide-initiated bulk polymerisation can be avoided by adding amines to the system (6). Retardation by oxygen of the initial rate of polymerisation has been studied in detail and is attributed to the formation of poly-peroxides (7). The pronounced 'gel-effect' in methyl methacrylate presents a major problem in controlling bulk polymerisations and several studies have provided quantitative information on the decrease in the termination rate constant which is responsible for this (8, 9). Cross-linking agents favour the earlier onset of the 'gel-effect' (8, 10) and this increases the difficulty of manufacturing materials which exploit the particular advantages of cross-linked sheet (e.g., improved thermal and solvent resistance). However, products with a limited degree of cross-linking are available for aircraft glazing, lens and watch-glass manufacture. Attempts have been made to produce sheets which can be both fabricated and cross-linked at the 'shaping' temperature ( $\sim 160^\circ$ ) using monomers which do not readily copolymerise with methacrylates at lower temperatures (e.g., triallyl cyanurate), but difficulties in curing the sheet either thermally or by radiation have not yet been completely overcome (11).

New moulding powders based on copolymers of methyl methacrylate with styrene (12) or  $\alpha$ -methylstyrene (13) have been introduced, the latter having a higher heat distortion temperature than have normal acrylic moulding powders. Methacrylates, with or without other monomers, can be polymerised in synthetic rubber latices to give rubber-resin blends, and this has been exploited to obtain moulding powders of greater impact resistance (14). Graft copolymers have been prepared by trans-esterification of polymethyl methacrylate with crystalline polyesters (15). Block copolymers can be prepared by mastication of mixtures of two polymers or a mixture of a monomer and a polymer (16), but no technically useful products are available as yet. Increased hardness and thermal resistance have been conferred on methacrylate polymers by uniform dispersion of fillers of small particle size (17).

Degradation of methacrylate homo- and co-polymers has been studied under a variety of conditions and as a result ultra-violet absorbers are now often included in clear sheet. Craze resistance can be substantially increased by biaxial stretching, which also gives a tougher sheet material useful for aircraft glazing (18). Methacrylate syrups for laminating glass-reinforced roof-lights were introduced in the U.S.A. two or three years ago (19), but are believed to have made little progress; no corresponding development has been announced elsewhere. Reinforcement by synthetic fibres has also been studied (20). Methacrylate monomers are used

at the 10–20% level to give improved outdoor performance in the better quality polyester/styrene resins for glass-reinforced translucent panels in the U.K. and more performance data have recently been published in the U.S.A. (21).

World production of acrylic sheet is now probably over 50,000 tons/year, largely by three major manufacturers. The traditional use in aircraft glazing is now only a minor proportion of the total market. Signs and displays account for 60–70% of the market in the U.S.A., but only 20–30% in Europe. Important outlets, some of which have been developed in Europe more than in the U.S., include lighting fittings, transport (windscreens), television set implosion guards, roof-lights, sinks and drainers. Other sanitary ware applications, e.g., baths and urinals, are likely to be of increasing importance. Shaping techniques have been given more attention (22) and there has been a noticeable trend towards greater mechanisation, particularly in the use of shaping/vacuum-forming machines. Acrylic sheet extruded from moulding powder has not so far reached any substantial tonnage except in Germany and Italy, although the proportion of acrylic moulding powders manufactured in Europe has recently increased considerably. Two significant advances in the U.K. have been the sale at a reduced price of clear polymer consisting of very small spherical particles, and the introduction of materials which are more thermally stable at injection moulding temperatures. Important applications of these products include rear-lights in motor cars, and, in the U.K. particularly, television set implosion guards, a new G.P.O. telephone hand-set and extruded lighting fittings and tubes.

In the United States emulsion paints based on methacrylate, acrylate copolymers are being increasingly used for exterior application on wood and masonry but have made less headway in Europe, where polyvinyl acetate-based paints are well established and are giving satisfactory service for both interior and exterior use. Acrylic solvent-soluble resins have been in use for some time as bases for solution paints for hard, glossy top finishes for refrigerators and cars, and a similar resin, which also gives a thermosetting finish, has now been introduced in water dispersion. Butadiene/methacrylate copolymers have established uses for paper coating (23), paper impregnation and leather finishing (24), while carboxylated rubbers are used in the new field of non-woven fabrics. Outside the paint field, the principal application for methacrylates solution polymers is as oil-additives. Copolymers of the higher-alkyl methacrylates have established uses, particularly as viscosity-index improvers in the 'multi-grade' oils (25). The more recently introduced 'detergent' additives which have sludge-dispersing properties are also based on methacrylate polymers and there is much patent activity on newer polymers with 'detergent' properties.

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## AMINOPLASTICS (D. N. Buttrey, M.Sc., F.R.I.C., F.P.I.)

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### Raw materials and resin development

A MAIN trend in the development of amino resins is towards lowering production costs, in particular of urea-formaldehyde (U.F.) resins, which have become highly competitive on a world scale, and melamine-formaldehyde (M.F.) resins. With U.F. resins this is being achieved by reduction of raw material costs and also numbers of types for bulk markets. Large users of M.F. resins are increasingly manufacturing their own condensation products where immediate use overcomes storage-life problems.

The more complex amino resins are finding applications in selective fields, e.g., textiles, paper, where specific properties cannot be obtained with the unmodified U.F. and M.F. resins.

An important move in the case of U.F. resins has been the adoption as a raw material of formaldehyde dissolved in aqueous urea solution, a typical product containing 59% formaldehyde, 26% urea and 15% water (1). Use of such concentrates lowers both carriage and dehydration costs in resin manufacture and minimises formaldehyde loss during resin dehydration.

The production of melamine from urea more cheaply has received continued attention, and an improved method of manufacture has been claimed (2) in which urea is pyrolysed to an intermediate product, which is then heated under high pressure. An alternative approach from ammonium thiocyanate has yielded several patents (3) and improved methods of purification have also been proposed, including a crystallisation process which gives 99.5% yield (4) and also sublimation (5).

The production of ethyleneurea from alkylene carbonate with  $\text{NH}_3$  at 200–290° has been described (6). Numerous patents for improved urea production have been published (see Supplementary Bibliography).

Continuous processes for making resins have also received attention. One such method uses three cylindrical containers for U.F. resin manufacture (7), and a second, for a range of resins including U.F., M.F. and dicyandiamide, employs a heated reaction tube (8).

Among potential interesting resin-forming materials that have

been advanced, condensation products of the triazine resin combined with other thermosetting resins, including U.F., to improve fire- and heat-resistance, have been investigated (9). They are also used for laminates and moulding (10), while diamino-triazines substituted by an aliphatic radical with 3-6 carbon atoms or cycloaliphatic or araliphatic radical of not more than 10 carbon atoms, are useful for laminating and surface coating resins, e.g., substituted guanamine (11a) and other triazine-formaldehyde resins (11b).

Polyureas, suitable for films, sheets and fibres, have been made from aromatic diamines and aromatic di-isocyanates (12). Dicyandiamide as a raw material continues to attract interest as it imparts fire resistance to laminating resins (discussed later), and also gives condensation products suitable for leather treatment (13).

### Application development

#### *Woodworking adhesives*

The world particle board industry has shown appreciable expansion and has become a major market for U.F. resins, which are largely sold as syrups with 70% resin content. Although the bulk of the industry is based on multiplaten press processes, extrusion processes are being used increasingly, e.g., the Kreibbaum process on which further development is improving performance (14). With the greater use of particle board in building, there is greater emphasis on fire-resisting qualities (15). U.F. resin-bonded flax-board is being used increasingly in furniture making.

U.F. resins remain the chief adhesives used for woodworking, furniture and interior-grade plywood, in spite of the more recent introduction of polyvinyl acetate adhesives. Improvement of U.F. adhesives is being effected by, e.g., the incorporation of free carboxylic acids of  $>16C$  atoms (16), and by the addition of dimethylformamide to reduce crazing of U.F. glues in gap-filled joints (17).

As a result of B.S. 1455:1956 and B.S. 1088:1957, all U.K. weather-proof plywood is now based on phenol-formaldehyde (P.F.) resin adhesives, which supersede melamine-fortified U.F. resins. Although satisfactory P.F. resins are available, the search for improved products continues, particularly for those which will reduce absorption into the wood during hot-pressing. One additive described is a silicate-methylolmelamine (18a). High polymeric substances, such as polyvinyl alcohol, are recommended as additives to both amino and phenolic resin adhesives to give a more stable viscosity/temperature relationship (18b).

#### **Paper treatment**

In the paper industry, anionic U.F. resins continue to dominate the wet-strength field, although there is increasing use of M.F.



resins applied as acid gels for higher wet-strength application, e.g., in photographic papers. Methods of preparing cationic U.F. resins have been described (19). The use of U.F. resin/starch adhesives and sizes in paper conversion is increasing, and adhesives based on U.F. resins containing amylopectin (20) and high-molecular-weight polyhydroxy or polyamino compounds, such as dextrin, pectin and alginates (21) have been patented. An interesting development is the use of polycondensation products based on urea, thiourea, biuret and *N*-alkyl- and *N*-aryl-ureas for paper filling to produce a voluminous paper, suitable for sound-absorbing, filtration or absorption requirements (22).

The market for paper-based decorative laminates continues to increase, and for surface-paper impregnation M.F. resin in spray-dried form or alternatively short storage life M.F. liquid resin, made by the user, continues to satisfy most of the market. The search for satisfactory stable liquid M.F. resins continues, recent developments including modification with thiourea (23, 24a), toluenesulphonamide (24b) and polyhydric aliphatic alcohols (24c). Cyclic ethyleneurea modification of M.F. resins is said to improve gloss, dimensional stability and abrasion resistance (24d), and a new process uses M.F. resin modified with polyvinyl acetate and glyoxal to impregnate fibrous sheets, which, after curing, are bonded with the same resin. The laminate is stated to be equivalent to conventional laminates of twice the thickness (25).

Non-woven fabric impregnated with M.F. resin is proposed as a surface laminating base to replace paper (26). Dicyandiamide-modified phenolic resin increases the fire-resistance of industrial and decorative base laminates (27). A new method of impregnating surface sheets of paper for decorative laminates is first to impregnate in a highly flowable resin containing buffers to retard hardening, e.g., borates, followed by impregnation of the same sheet in a low flowable resin, highly precondensed, and containing a latent hot hardener, e.g., an ammonium salt of an acid (28); no overlay paper is necessary.

### Textile finishing

In the textile field, dimethylolurea (D.M.U.) is still largely made by users for crease-resisting fabrics. For drip-dry finishes, where chlorine resistance is important, a steady increase in the use of dimethylolmethylethyleneurea (D.M.E.U.) is noted, and also blends of this substance with melamine resin. D.M.E.U./butadiene-acrylonitrile latex mixture improves the compressional resistance of cotton carpet yarns (29). Triazine compounds are also finding increased use for imparting crease-resistance (30a); propyleneurea has been described for the same purpose (31b). The newer resins have been discussed with particular reference to chlorine absorption and subsequent damage to fabrics (31); U.F., M.F. and cyclic ureas

are considered, also polyglycol acetals and epoxy resins. For stiffening rayon, nylon and other fabrics, U.F. precondensed resins are finding increased use as additives for crease-resistance and for direct applications; there is certain use of D.M.U. ethers for non-woven fabrics, although in this field butadiene compounds are often preferred. M.F. resins continue to be more important than U.F. resins in glazing applications, particularly for permanent embossing on cotton. There is still a limited use of U.F. resins in starch sizes, although these are being displaced by other polymeric materials.

### Miscellaneous

The use of rigid foams based on U.F. resins has achieved some prominence in the technical literature (32, 33), particularly for *in situ* foaming in cavity walls of buildings. Such foams are stated to be mainly open-cell, and thermal conductivities of 0.023–0.30 kcal./mh<sup>2</sup>c at 20° are reported (approaching maximum value of 0.022 kcal./mh<sup>2</sup>c for still air). Tests have shown the foams suitable for use up to a temperature of 120° (32). It is stated that 27,000 sites in north European countries have been sprayed with such resin foam, and a system is now available for use in the U.K. (34). The extension of the process to fire-fighting, particularly in mines, has been proposed (35).

Some interesting applications are the production of fire-lighters based on hardened U.F., paraffin emulsion, arising out of an earlier patent on solid resin/organic liquid emulsified systems (36), and fertilisers for turf based on high U.F. ratio condensation products (37). A U.F. condensate has also been found to be a promising control for potato scab (38).

### Moulding compositions

There has been a general revival of the use of U.F. moulding powder, largely attributed to improvements in moulding equipment rather than in chemical composition. During the past two years moulding processes have become more fully automatic, whereas they were previously dependent largely on individually-manned presses. The improvements have been made to meet competition from thermoplastics. For large U.F. mouldings, improved gloss and reduction of gassing and flow-lines is obtained with a blend of two resins of different U.F. ratios (39).

Melamine fortification of U.F. moulding powders is being increasingly used to meet specific requirements, and a new development is in melamine-fortified P.F. moulding powders, which are stated to combine the colour properties of wood-flour-filled M.F. moulding powder with the physical properties of P.F. moulding powder.

With the interest in M.F. moulding powders, the emphasis on improvement in performance has been stressed, particularly reduc-

tion of shrinkage, for which addition of the condensation products of *N*-arylbiquanide has been proposed (40); equipment to measure such shrinkage has been described (41).

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#### Raw materials

##### *Urea manufacture*

Oriental High Pressure Industries Co., Ger. P. 1,006,851; Stamicarbon N.V., B.P. 819,030; 822,149; Ger. P. 958,481; Pechiney Cie de Produits Chimiques et Electrometallurgiques, U.S.P. 2,904,393; Vilesov, G. I., *et al.*, Russ. P. 122,149; Belonov, I. P., Russ. P. 116,513; Hydrocarbon Research Inc., U.S.P. 2,913,493; Monsanto Chemical Co., B.P. 818,864; Badische Anilin- u. Soda-Fabrik A.-G., Ger. P. 1,024,533

##### *Substituted ureas*

Du Pont de Nemours & Co., E. I., B.P. 811,681; Rohm & Haas Co., U.S.P. 2,891,944

##### *Buret from urea*

Stamicarbon N.V., B.P. 830,114

##### *Melamine manufacture:*

from ammonium rhodamide and ammonia. Bergwerksverband G.m.b.H., Ger. P. 1,000,385  
 from SO<sub>2</sub>, guanidine sulphamate and urea. Consolidated Mining & Smelting Co. of Canada, Ltd., Canad. P. 579,563  
 from dicyandiamide. Société des Produits Azotés, Fr. P. 1,161,862-3; B.P. 814,934; Neubner, R., U.S.P. 2,913,461

#### Condensation products

##### *Surface coatings*

Aminoplast resin emulsions. CIBA Ltd., Ger. P. 1,012,067  
 U.F. cycloaliphatic ketone resin condensates. VEB Leuna-Werke 'Walter Ulbricht', Ger. P. 1,016,440  
 Amino polyamides, P.F. resins. General Mills Inc., U.S.P. 2,891,923

##### *Adhesives*

U.F. polymethylenetetramine condensate. Deutsche Gold- u. Silber-Scheideanstalt, Ger. P. 965,766  
 Amino resin/polyvinyl acetal composition. Siemens-Schuckertwerke A.-G., Ger. P. 1,005,666

##### *Moulding compositions*

M.F./thiourea. Chemische Werke Albert, Ger. P. 1,006,150  
 Amino resin/benzenemonosulphonic acid polyhydric alcohol modified. CIBA Ltd., Ger. P. 1,014,320

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#### *Analysis and testing*

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Solids content of U.F. resins. Decléman, P. R., & Van der Schee, A. Ch., *Vestník*, 1959, **32**, 261

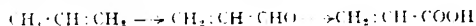
### ACRYLIC RESINS (D. M. Woodford, M.A.)

*Scott Bader & Co. Ltd., Wollaston, Northants*

ACRYLIC resins have useful properties; their resistance to light and weather is unsurpassed and their low temperature flexibility is very good. In the past their use has been limited by price and their thermoplastic nature, but new methods of production are now giving cheaper monomers and new polymerisation techniques can give polymers with any required degree of thermoplasticity. With the removal of the two drawbacks mentioned, the consumption of acrylics is now expanding rapidly.

#### **Monomers**

Historically, the lower acrylate esters have been produced from acetylene and from ethylene oxide (1, 2), but a more recent route is from ketene via  $\beta$ -propiolactone (3). A route which is being actively explored, but which is not yet in commercial production, is the catalytic oxidation of propylene:



If this route proves practicable, very cheap acrylic monomers are possible. Other sources which have been discussed include acrylonitrile (4), lactic acid (5), ethoxypropionic acid (6), from corresponding saturated esters (7), and chloropropionates (8), maleic acid (9), caprolactone (10), acyloxypropionic acid (11), ketene and formaldehyde (12), succinic anhydride (13).

Acrylamide is now available in bulk and is finding a wide range of uses by reason of the reactive groups left after ethylenic polymerisation, which may both provide a site for cross-linking reactions and confer water solubility on the polymer. The amide is normally produced by the hydrolysis of acrylonitrile (14).

Other monomers which have aroused special interest are: hydroxyalkyl acrylates (15, 16) and chloroacrylic esters (17, 18).

### Polymerisation

Most acrylic polymers are produced and used in emulsion, although solution and suspension techniques are also used, but rarely bulk polymerisation. Although the basic techniques of polymerisation by free-radical-type initiation are well established, some new catalyst systems have been suggested; they include drier metal salts (19), nascent hydrogen (20), a tertiary amine oxide (21) and saccharin salts (22). Work has also been done on the possibility of polymerisation in emulsion with little or no emulsifier present (23), or with a reactive emulsifier (24), and on photopolymerisation (25, 26). An interesting technique for polymerising water-soluble monomers in a water in oil emulsion is also reported (27). Crystalline polyacrylates have been produced experimentally (28).

Considerable work has been done on grafting reactions but the grafts obtained do not appear to be commercially very important.

The major field of work in acrylic polymerisations has been on cross-linking reactions and it seems probable that in the future most acrylic polymers will be cross-linking types, especially if a good air-drying system can be developed. It is convenient to classify the types of cross-linking by the reactive groups in the main polymer chain. Many are possible, but the following are some of the most important.

(1) *Carboxyl groups*, which can be interacted with, among others, phenol (29), amino-formaldehyde resins (30) or epoxides (31). The carboxyl groups may also be ionically cross-linked with a polyvalent metal ion (32).

(2) *Hydroxyl groups* may be reacted with similar reactive cross-linking agents (33).

(3) *Amide groups* can be cross-linked with a variety of di- or poly-functional agents, including glyoxal (34) and polyisocyanates (35). They may also be methylolated and further etherified. These methylol or etherified methylol acrylamide groups will react together on heating, preferably in acid conditions (36). The -OH of methylolacrylamide can also take part in the reactions discussed under (1), and acrylamide itself will cross-link by imide formation when heated strongly (37).

(4) *Epoxy groups* may be reacted with each other (38), or with polyfunctional compounds containing reactive hydrogen atoms such as acids (39), 'precondensate' resins (40a), etc. They are reasonably stable to water and can be used in emulsion form. Water solutions of phosphate esters may be used (40b) and epoxy and other reactive groups introduced to the same polymer chain (41).

(5) *Isocyanate esters* of unsaturated acids may be copolymerised even in emulsion. The polymers are cross-linked by heating or by compounds containing reactive hydrogen (42).

(6) *Unsaturated groups*. When a diene is used in polymerisation

the residual unsaturation may be used to give further cross-linking, as in the vulcanisation of rubber or cross-linking of butadiene-styrene emulsions for metal coating.

### Applications

In the U.S.A. the annual consumption of acrylic esters in million lb. is: paint 30, fibres 8, leather 7, speciality plastics 6, textiles 5, paper 4, polish 4, adhesives 1, others 1 (43). In this country the figures are not available but, apart from paints, the pattern is probably very similar. The use in fibres, though considerable, is outside the scope of this article (see 'Synthetic Fibres').

No significant quantity of acrylic emulsion paint is made in this country, although various speciality paints are made. Metal finishes are now gaining acceptance, the 'Scopacron' range (Styrene Copolymers) being notable. Such finishes may also be applied in emulsion form (44). Acrylates are also finding increasing use as co-monomers in vinyl acetate emulsions, although the advantages of such systems have been questioned (45).

Leather-finishing techniques are already well established and work has chiefly been concentrated on improving toughness by cross-linking (46a) and adhesion by incorporating hydroxy groups or ureide groups (46b).

In textiles, the major work has been on the improvement of acrylic binders for non-woven fabrics (the Supplementary Bibliography gives some references). An interesting fluoroacrylate for water- and oil-proofing fabric is also reported (47).

There has been considerable work in the field of water-soluble polymers, which are used in thickening agents, textile sizes, soil-suspending agents for detergents, soil stabilisers and bonding agents for ceramics (see Supplementary Bibliography for references). One of the applications which is expected to grow very rapidly is in dry bright floor finishes, for which products of high molecular weight with fine particle size are used in emulsion form (48).

Other interesting applications include cyanoacrylate monomers as adhesives with unique properties (49), the use of graft polymers in pressure-sensitive adhesives (50) and acrylates for plasticising and reinforcing polyvinyl chloride (51).

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- Cement improver. American Cyanamid Co., U.S.P. 2,868,753
- Paper additives. American Cyanamid Co., U.S.P. 2,890,978
- Drilling mud conditioner. Monsanto Chemical Co., Canad. P. 594,858
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## INORGANIC AND SEMI-INORGANIC POLYMERS

(W. Gerrard, D.Sc., Ph.D., A.R.I.C.)

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RECENT demands for polymeric material complying with exacting specifications of resistance to heat (500°), oxidation and hydrolysis, have encouraged considerable activity in the search for inorganic back-bone polymers. Expressions such as 'heat-resisting' and 'inorganic' polymers are appearing more and more frequently, and at this stage of development it is well to keep in mind certain formal designations or definitions. Materials referred to as 'inorganic polymers' frequently comprise an inorganic back-bone or three-dimensional net-work skeleton with organic (often alkyl or aryl) groups attached. On the other hand, phosphonitrilic chloride,  $(\text{PNCl}_2)_n$ , is an example of a truly inorganic polymer. At the present time there is a danger of jumping to conclusions on glancing at reports on unfinished researches, because of the indiscriminate implications of the expressions mentioned above. It is often far from clear in these reports whether the materials made are likely to be *applicable* to the technical service stated. At this fluid stage of development extreme caution should be exercised before associating a particular polymer with a specific application. Although the polymers produced in a research project may be interesting, and even have definite potentialities, in most cases precise applications have yet to be established. Project policy has been hovering uncertainly between frantic product-searching and the more sedate scrutiny of factors influencing the formation of polymer units and the bond properties involved. There are those who emphasise the need for reliable data on heats of formation and bond energies.

In assessing the potential applicability of inorganic polymers referred to in a report, the chance of upscaling the production must

be weighed, for much experimentation has been on small fractions of a molal scale. This may be due to bench convenience, but if it is imposed by a restricted supply of starting reagents, the whole project must be assessed in terms of these. Nevertheless, there are recent examples of a starting material, formerly in restricted supply, quickly becoming commercially available because of some other development. This has recently been so of diborane, which has very attractive potentialities in the field of inorganic polymers.

Little more can be attempted in this review than to draw attention to systems which have been reported as being under examination. The siloxane systems as such have been omitted, because these are well established, and their asymptotic limitations would appear to be essentially known.

Recently, a review (1) on inorganic polymers dealt with the general chemistry of a number of systems, and another (2) on the experimental approach to boron polymers outlined the essential points involved in the search for applicable inorganic polymers in general.

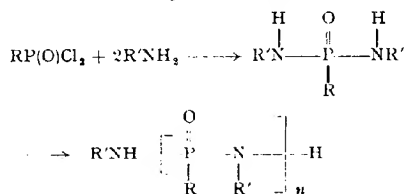
### Phosphonitrilic chloride system

Phosphonitrilic chloride has been known for over a century; the essential fundamental knowledge of its polymeric constitution as  $(\text{PNCl}_2)_n$  has been known for some time (3), and comments on the oily, waxy and rubbery consistency are to be found. The potentialities of this system in providing a great variety of derivatives, each entailing application of the modern physico-chemical techniques for determination of structural and bonding features, are prolific, and under the encouragement of sponsors of high-temperature-polymer projects, the amount of published work is rapidly increasing. Nevertheless it is not at all clear if any of these polymers have commercial applications, although their flame-proofing properties appear to be established (4, 5).

Materials suitable for gaskets, insulators and packings for use at temperatures up to  $500^\circ$  have been produced from asbestos and polyphosphonitrilic chloride  $(\text{PNCl}_2)_n$  ( $n=3-6$ ) (6). The hexaisothiocyanate derivative polymerises to an elastomer (7), and the chlorides with chain structure  $-(\text{NPNCl}_2)_n-$  ( $n=\text{e.g., } 10$ ) have been obtained (8). With a small amount of water they gave latex-like material. Materials of the type  $(\text{R}_2\text{PN})_x$ , where  $x=3$  or 4, and R is an aryl group, are prepared by the reaction  $x(\text{R}_2\text{PN}_3) + x\text{NH}_4\text{X} \rightarrow (\text{R}_2\text{PN})_x + 4x\text{HX}$ , where X=halogen, and have high thermal and chemical stability (9). Highly polymeric compounds  $(\text{PN}_2\text{H})_x$  are obtained by heating phosphonitrilamides obtained from the trimeric and tetrameric phosphonitrilic chlorides and liquid ammonia under pressure (10). Polymers of the type  $(\text{HN:PNEt}_2)_x$  have been reported (11).

**Phosphorus-nitrogen-oxygen (PON) polymers**

Resins obtained by the condensation of phosphonic diamides appear promising (12, 13), but proper assessment as to their use as structural materials has not yet been described.

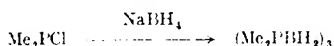


The non-volatile and insoluble phosphorus oxynitride (PON)<sub>n</sub> is evidently a completely cross-linked polymer with potentialities in the field of ceramics (14).

**Phosphinoborine polymers**

The original (15) production of 'resins', e.g. (Me<sub>2</sub>PBH<sub>2</sub>)<sub>3</sub>, described as having promising heat and chemical stability, was based on diborane and its simple alkyl derivatives. Many very interesting variations in the groups attached to phosphorus and to boron are dealt with in several subsequent publications, but the application of the products has been little discussed.

Two outstanding features recently developed (16-20) are the introduction of the CF<sub>3</sub> group, e.g. in [(CF<sub>3</sub>)<sub>2</sub>PBH<sub>2</sub>]<sub>3</sub>, and the insertion of the boron moiety by a comparatively simple reduction of a dialkyl or diarylphosphinyl halide by sodium borohydride in diethylene glycol dimethyl ether.

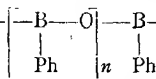


The production of diborane for direct reaction with dialkyl- or diaryl-phosphines, R<sub>2</sub>PBH, can now be carried out easily by ordinary bench techniques, and investigations in this field have been greatly simplified. In recent reports the phosphinoborines are stated to have plastic consistency, excellent heat resistance, chemical stability and dielectric properties. Some are suitable as hydraulic fluids. The cyclohexyl member [(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>PBH<sub>2</sub>]<sub>3</sub> is suggested as a dielectric (18).

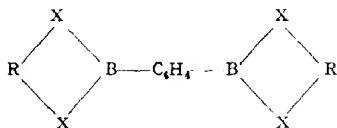
**Boron polymers**

The position at the beginning of 1959 has been critically reviewed (2). Three outstanding features at present are the relative ease of hydrolysis of boron-oxygen links, the tendency to oxidative fission of boron-carbon links, and the trimeric ring-forming propensity;

which for example prevents phenylboronic acid,  $\text{PhB(OH)}_2$ , from polycondensing to  $\text{HO}-\left[ \text{B}(\text{Ph})\text{O} \right]_n-\text{B}-\text{OH}$ , analogous to the

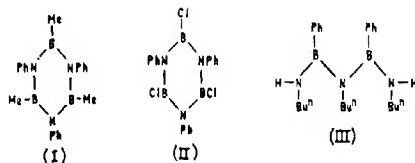


siloxane system. *p*-Phenylenediboronic acid,  $(\text{HO})_2\text{B}\cdot\text{C}_6\text{H}_4\cdot\text{B(OH)}_2$ , (21, 22) would appear to offer possibilities, but the tendency for ring formation on the boron is still present, and the very interesting structures investigated (23), represented as shown ( $\text{X}=\text{O}$  or  $\text{N}$ )



are heavily weighted with organic groups, and do not appear to show clear prospects of reaching the required specifications. The corresponding diboron compounds with, for example,  $(\text{CH}_2)_n$  in place of  $\text{C}_6\text{H}_4$  offer no material advantage as yet. In this connexion diboron tetrachloride ( $\text{B}_2\text{Cl}_4$ ) (24, 25) would be a very attractive reagent if its preparation could be considerably improved. An entirely different aspect is afforded by the example of the carbon-carbon polymerisation of *p*-vinylphenylboronic acid,  $p\text{-CH}_2\text{:CH}\cdot\text{C}_6\text{H}_4\cdot\text{B(OH)}_2$ , to a white, air-stable powder which did not melt below  $300^\circ$  (26).

Experimentation in the borazole ( $\text{HB}\cdot\text{NH}$ )<sub>3</sub> systems has been considerably expedited by convenient kilogramme-scale production not only of *B*-trichloroborazole and the *N*-alkyl and *N*-aryl derivatives, but especially of phenylboron dichloride (and *n*-butylboron dichloride) (2, 27). The borazole systems are potentially good for specific investigation. Current projects (28-30) are the study of the separate reactions leading to the borazole structures, the evaluation of the influence of substituents on hydrolytic and thermal stability and on mechanical properties, and the discovery of means of obtaining chains either by preventing formation of the trimeric structure or by linking the trimers together. The following have been investigated. (I) has good hydrolytic stability, (II) undergoes dehydrochlorination on heating ( $300\text{--}450^\circ$ ) and at  $470^\circ$



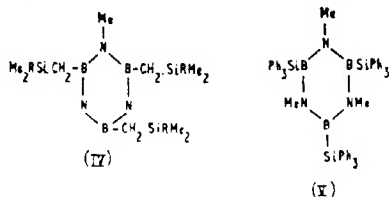
gives a mobile liquid which sets to a dark brown solid on cooling, and becomes a black, brittle, chemically stable solid at 600°. On being heated (III) undergoes polycondensation by elimination of *n*-butylamine and gives liquids and a solid, probably comprising chains instead of borazole rings. Aminopolyborazoles are formed by eliminating amine from the *B*-alkylaminoborazoles. *p*-Phenylenediamine and boron trichloride give intractable solids due to excessive cross-linking.

A new borazole system (28) is based on the previous prototype development of an  $\text{M}-\text{O}-\text{M}'$  polymer ( $\text{M}=\text{B}$ ,  $\text{M}'=\text{P}$ ) by the elimination of alkyl chloride from the 1 : 1 complex of boron trichloride and a trialkyl phosphate (31). The *B*-trichloroborazole-triethyl phosphate complex gave first alkyl chloride, and then ethyl phosphate and a solid *B*-mono-alkoxyphosphoryl polyborazole which on further heating to 800° was converted into a purely

inorganic polymer probably containing the skeleton  $\begin{array}{c} \text{O} \\ | \\ -\text{N}-\text{B}-\text{O}-\text{P}- \end{array}$ .

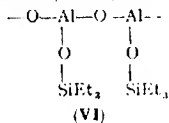
The evaluation of these materials has still to be effected.

Organosilicon-substituted borazoles (32-34) have been prepared. In (IV) when  $\text{R}=\text{Me}$ , the compound is stable to alkaline hydrogen peroxide at room temperature, and when  $\text{R}=\text{Me}_3\text{SiO}$ , the compound is stable to air oxidation and hydrolysis under mild conditions. When the group attached to boron is  $\text{OSiMe}_3$ , the compound is not hydrolytically stable. The *B*-tris(triphenylsilyl)-compound (V), a yellow, highly viscous oil (or, according to another worker, crystalline), was found to be stable to dry air, but readily susceptible to hydrolysis, which caused fission of the  $\text{B}-\text{Si}$  link.



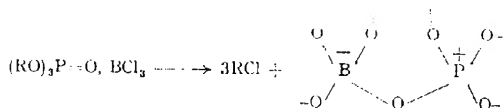
### M-O-M' polymers

Prolific researches have involved the development of what may be termed  $\text{M}-\text{O}-\text{M}'$  or mixed anhydride polymers, including many papers from Russian workers (35-38) on structures typified by (VI).

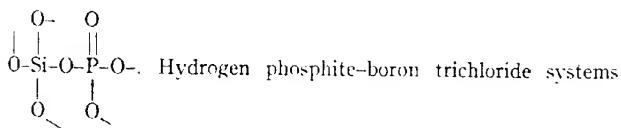


Silicon can alternate with aluminium to give an Al-O-Si backbone, and phenyl can take the place of ethyl. Such polymers are solids which harden on heating, the ethyl polymer faster than the phenyl one. Titanium, tin and boron can also be incorporated in the backbone. Details of their application are far from clear from the literature. Thermal breakdown and oxidation tests (39) seem to refer to the thermoplasticity of films on metallic supports, for example when applied as dielectrics in machines and apparatus for long service in the atmosphere at temperatures above 130°. In general, thermal oxidation by destruction involves the pendant organic groups, and results in cross-linking of the 'M' atoms through oxygen.

An entirely different approach to M-O-M' polymers has been made from a different starting point (31). A complex of a trialkyl phosphate and boron trichloride first formed eliminates alkyl chloride and develops a solid polymeric material, which finally becomes boron phosphate.



Likewise a trialkyl phosphate and silicon tetrachloride (40) give alkyl chloride and silicon phosphate having a network based on



have also been studied (41). The probable extensions of these prototype reactions are obvious.

### Other systems

Studies on the -(Si-N-Si-N)- backbone systems have led to the preparation of compounds having the -SiH<sub>2</sub>NMe- grouping, with about 20 units in a chain (42). Chemical and thermal stability have been evaluated, but applicability has not been assessed. Certain organo-arsenical polymers have similarly been prepared and studied (43). Organophosphorus polyesters related to the 'phoryl resins', which have been known for 10 years, and also organophosphorus polyamides and polyurethanes, have been reviewed (44). Sulphur nitride polymers are attracting some attention (45).

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## POLYMERS AND COPOLYMERS OF STYRENE AND ITS DERIVATIVES (H. B. Hopkins, B.Sc., Ph.D., F.R.I.C.)

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### General

THE production of polystyrene in the United Kingdom increased from 22,900 tons in 1956 to 39,000 tons in 1959 (1), and the production capacity is now estimated to be of the order of 60,000 tons. Impact-resistant or toughened grades have constituted an increasing proportion of total output. This proportion has risen to about 40% in the U.K. (1) and 50% in the U.S.A. (2). In 1958, the end-use pattern in Britain of polystyrene was as follows (3): refrigerator parts, 23%; housewares, 14%; toys and games, 12%;



electrical items, including radios and gramophones, 15%; packaging, 16%; extruded sheet (other than for refrigerators) 8%; shoe heels, 5%; expanded materials, 3%; wall tiles, 1%; miscellaneous, 3%. A similar pattern prevailed in 1959 (1), except that greater use was made of toughened, as opposed to general-purpose, material.

### Polymerisation and polymer properties

#### *Untoughened styrene and substituted styrene polymers*

Much work has been published on the subject of stereospecific polymerisation (4, 5), but no commercially useful polystyrene appears to be in production by this means. Integrated processes have been developed for the conversion of ethylbenzene, contained in a petroleum xylene fraction, to polystyrene. The polymerisation is effected either by an aqueous suspension method (6) or by the use of a sodium dispersion (7). In the latter case, separation and purification of the ethylbenzene and the monomeric styrene are unnecessary. In another type of continuous process, unpurified styrene is polymerised in bulk to 70% conversion, the excess of monomer and the volatile impurities being removed in a devolatilising extruder (8).

In radical-initiated polymerisations, a more rapid reaction results from the use of a mixture of two catalysts, benzoyl peroxide and *t*-butyl perbenzoate, in conjunction with progressively increasing temperatures in the range 100–135° (9). The unsaturated dimer of  $\alpha$ -methylstyrene acts as an effective chain-transfer agent (10). Polystyrene of high molecular weight may be produced rapidly at moderate temperatures ( $\sim 60^\circ$ ) by the action of a small amount of sodium promoted by a dialkyl ether of a dihydric alcohol (11). Polystyrene of good colour, clarity and electrical properties and high softening point may be produced by an emulsion technique with hydrogen peroxide as the initiator and a quaternary ammonium salt as the emulsifying agent (12).

Polymers of high softening point may be prepared by conventional methods from certain ring-alkylated styrenes, particularly *p*-*t*-butylstyrene (130°) and *o*-methylstyrene (111°) (13, 14). Commercial polymers derived from these monomers are not available, but a process for the manufacture of *o*-methylstyrene has been described (15). A poly-methylstyrene that was introduced to the market in 1958 (16) has since been withdrawn. Polymerisation of  $\alpha$ -methylstyrene at 25°, with a reaction period of 30 min., in the presence of sodium and tetrahydrofuran has given a high-molecular-weight polymer with the high softening point of 165°. By a similar technique, equal weights of styrene and  $\alpha$ -methylstyrene gave a polymer with a softening point of 130° (17). This value may be contrasted with the softening point of 108° reported

for a 22.5 : 77.5  $\alpha$ -methylstyrene/styrene copolymer produced by a radical-initiated reaction.

A novel development has been the introduction of lithium atoms into polystyrene (18, 19). The inclusion of a long-chain fatty acid in a mass polymerisation is said to improve the physical properties of the polymer and the surface gloss of moulded articles (20). The incorporation of tetramethyldiaminopropanol has been recommended to minimise the degradation of polystyrene on weathering (21). The accumulation of electrostatic charge may be prevented by the incorporation of a minor proportion of a compatible polar organic compound of low volatility, such as *NNN'*-tetra-(2-hydroxypropyl)ethylenediamine (22). Direct halogenation of polystyrene has been suggested as a means of conferring flame-retardant properties on the polymer (23). Other flame-proofing methods have included the incorporation of a bromo-alcohol derivative (24) or of highly chlorinated organic compounds in conjunction with an antimony compound (25). Water-soluble styrene polymers, useful, for example, as sizing agents, are obtained by direct sulphonation (26).

Improved flow properties during moulding result from the inclusion of a proportion of low-molecular-weight polystyrene (27). A correlation between molecular structure and rheological properties has been reported (28).

#### *Untoughened copolymers*

Copolymerisation of styrene with acrylic monomers, such as methyl methacrylate or acrylonitrile, gives rise to products with higher softening points and greater hardness, toughness and chemical resistance compared with polystyrene itself. On the other hand, the presence of styrene in the copolymer confers easier processability and a lower price compared with polymers formed from the acrylic monomers alone. The weight ratio of the comonomers in the polymerisation charge and the degree of conversion of monomer to polymer have to be carefully controlled if the desired homogeneous, i.e., optically clear, copolymer is to result. Numerous copolymers of this general type have been described.

A styrene-methyl methacrylate copolymer is available commercially (29). A new process for the production of such a copolymer involves the continuous addition of monomers to, and removal of polymer/monomer solution from, a coil-shaped reactor in which the composition of the contents is maintained at a constant value. In this manner, variations in the composition and molecular weight of the product are minimised (30*a*). A styrene-acrylic acid copolymer may be similarly prepared (30*b*). The properties and applications of a styrene-methyl methacrylate copolymer have been compared with those of polystyrene and of polymethyl

methacrylate (31). The copolymer has good light stability over a long period, in contrast to the usual grades of polystyrene. A copolymer of  $\alpha$ -methylstyrene and methyl methacrylate has also been produced (32).

Copolymers of styrene and acrylonitrile have been available for a few years (33). The replacement of styrene in the copolymer by  $\alpha$ -methylstyrene leads to a further rise in the softening point of the material (34). Other combinations have included a terpolymer prepared from styrene,  $\alpha$ -methylstyrene and methacrylic acid (35a) and an  $\alpha$ -methylstyrene, acrylonitrile, alkyl methacrylate terpolymer (35b). A styrene-dimethyl itaconate copolymer and a terpolymer of these two monomers with acrylonitrile are being produced in Italy. The properties of these polymers have been stated to be superior to those of polystyrene and comparable with those of polymethyl methacrylate (36). Styrene may be polymerised by means of a sodium naphthalene derivative to give a 'living' polymer which may subsequently be used to initiate the polymerisation of another monomer. A block copolymer is thereby obtained (37). Active centres may be induced in a polymer by the action of ozone (38), a polymerisation initiator (39a) or radiation (39b). Polymerisation of a monomer subsequently added may be initiated at these centres to furnish a graft polymer.

#### *Toughened polymers and copolymers*

A detailed examination of the function of rubbers in toughening thermoplastic polymers has been reported (40). The incorporation of a rubber into styrene polymers or copolymers may be brought about by one of two general methods. In the first, the two components are intimately mixed together, for example, by direct blending on a mill or by coagulation of a mixture of polystyrene latex with a rubber latex. The second method involves the polymerisation of a solution of the rubber in styrene monomer. At the end of the polymerisation the rubber is present in the form of very small particles which are dispersed throughout the polymer.

Improvements in toughened materials produced by the blending method have been concerned mainly, as in the case of untoughened polymers, with the use of copolymers of greater chemical resistance, greater strength and higher softening point than polystyrene. A material of high impact strength is formed by blending an  $\alpha$ -methylstyrene, acrylonitrile copolymer with a butadiene/ $\alpha$ -methylstyrene rubber on to which has been grafted, for example, a methacrylic ester (41). Another typical toughened product is formed by blending 80 parts of an 80 : 20 methyl methacrylate  $\alpha$ -methylstyrene copolymer with 20 parts of a 70 : 30 butadiene styrene rubber (42).

The bulk polymerisation of solutions of rubber in styrene is well known, but suspension techniques have been described recently

(43). The stabilised aqueous suspension is usually formed after partial conversion of the monomer to polymer.

The toughening agents employed have included polyethylene (44) in addition to the usual butadiene-styrene copolymers or polybutadiene.

Materials that have assumed increasing importance in view of their exceptional strength and high chemical resistance are the so-called 'A.B.S.' polymers (acrylonitrile-butadiene-styrene), the properties of which have been reviewed (45). Styrene and acrylonitrile monomers may be polymerised in a polybutadiene latex (46a). Variations have included the replacement of acrylonitrile by methacrylonitrile (47) or acrylic acid (46b). A three-component blend, derived from a butadiene-acrylonitrile copolymer, a styrene-acrylonitrile copolymer and polyvinyl chloride, has been patented (46c).

Since a rubber-toughened thermoplastic is a two-phase system, the material will be opaque or translucent, unless the refractive indices of the two phases are almost identical, which is not usual. By suitable adjustment of the monomer ratios in the two components, a transparent toughened styrene copolymer may be obtained (48a). The relatively large difference between the refractive indices of polybutadiene and polystyrene makes it necessary that the rubber should contain a considerable proportion of bound styrene and the resin component an appreciable proportion of a co-monomer with a refractive index lower than that of styrene.

Toughened styrene polymers may be stabilised against the action of heat and light by the incorporation of a compound such as tetra(hydroxypropyl)ethylenediamine (48b).

### Applications

#### *Extruded sheets*

The strength of extruded film and sheet may be increased by stretching simultaneously in the direction of flow and transversely in the same plane. The properties of mono- and bi-axially oriented sheet and film have been compared with those of unoriented materials (49). Methods for the heat-forming of toughened sheet have been examined in detail (50). Vacuum-forming techniques are now in general use. Sheet with improved surface texture is obtained if the sheet is quenched by a current of cool gas on leaving the die (51).

The use of polystyrene in the production of microporous sheets and films for use as battery separators has been studied (52).

#### *Moulding*

The most notable advance has been in the size of articles formed by injection moulding. This development has been facilitated by

the use of pre-plasticising equipment which enables a heavier moulding to be obtained in a given time from a given machine. Large refrigerator liners are being manufactured at a high output rate (53). The development of copolymers of styrene with acrylic monomers, referred to previously, has permitted the moulding of articles such as oil-filter bowls, furniture polish containers, tumblers, cutlery handles, outdoor display signs and vending machine windows for which polystyrene itself would be unsuitable on account of inadequate light- or chemical-resistance.

The production of the exceptionally tough A.B.S. polymers in the U.S.A. in 1959 constituted about 6% of the total output of polystyrene moulding materials (2). A particular use has been in piping and pipe fittings (53a).

#### *Expanded materials*

The potential consumption of polystyrene in this application is very considerable and large developments are probable in this field. The production of expandable polystyrene involves the incorporation within the polymer of a volatile material or 'blowing agent'. When the temperature is raised, the blowing agent, now in gaseous form, brings about an expansion of the softened polymer, which thereby assumes a sponge-like structure. Dichlorodifluoromethane (54a) or pentane (54b) constitute suitable blowing agents. Very small pores are obtained if carbon dioxide is also included (55). Another method involves the addition of an epoxy resin and a curing agent to the beads of expandable polystyrene. The heat evolved on curing brings about expansion of the polymer (56). A technique for the production of foamed polystyrene of exceptionally low density involves partial expansion of the beads without mutual fusion by means of steam, followed by further expansion to yield an integral foam (57). Copolymers of styrene with a small amount of divinylbenzene give expanded material which is more resistant to collapse of the cellular structure than that formed from polystyrene alone (58). The continuous extrusion of expanded polystyrene sheet has been described (59a). The polystyrene used may be toughened (59b), coloured (59c) or fire-resistant (60).

The principal outlet for expanded polystyrene has been in thermal insulation, particularly in refrigeration (61) and in building (62). Articles such as portable refrigerators, ice-buckets and insulated jugs are now being manufactured solely from expanded polystyrene. Larger thermally insulated containers consist of foamed polystyrene with inner and outer shells made from A.B.S. polymer (63). In building, slabs of polystyrene foam form an effective barrier against the entrance of moisture and the loss of heat (64). Chair frames have been manufactured from this material (65).

*Packaging*

Disposable food containers are being produced by a variety of methods (66). Thin-wall articles such as drinking cups and processed cheese containers are being produced by injection moulding or vacuum forming of toughened polystyrene. The latter technique is also employed in the manufacture of thin-wall trays for food-stuffs. Compared with waxed paper, the plastic articles have the advantage of good appearance, greater hygiene and non-absorbance of liquids. Medium-wall food containers are being moulded in untoughened material, and injection-moulded fruit punnets are also used. Disposable fruit-squash containers, moulded in toughened polystyrene, have recently made their appearance. Paper-thin expanded polymer has been produced (67) and has been utilised in the manufacture of rigid cups with a thin, impervious inner surface (68).

Expanded polystyrene is used for the cushioning of fragile articles in transit (69), and biaxially oriented film is used in the packaging of food and clothes (70).

*Miscellaneous*

Polystyrene has found a use in lighting fixtures, gramophone records and cement compositions, while the toughened polymer has found an outlet in shoe heels, particularly of the stiletto type.

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**Appendix I***Production of styrene polymers*

No.	Catalyst or type of process	Patent No.	Patentee
1	Ziegler-type	B.P. 826,021; 844,844; 847,102	Montecatini Soc. Gen.
2	" "	B.P. 808,132; 812,178	Imperial Chemical Industries Ltd.
3	Sodium-alkenyl	U.S.P. 2,841,574	Ethyl Corp.
4	Metal oxide	B.P. 851,657	American Cyanamid Co.
5	Suspension	U.S.P. 2,719,143	Shell Chemical Co.
6	"	U.S.P. 2,934,559	Dow Chemical Co.
7	"	B.P. 802,061-2	" "
8	"	B.P. 853,318	Monsanto Chemical Co.

**Appendix II***Polystyrene with anti-static properties*

No.	Additive	Patent No.	Patentee
9	Quaternary ammonium compounds	U.S.P. 2,850,517; 2,891,878	American Cyanamid Co.
10	Polyhydric polyester	B.P. 781,177	Styrene Products Ltd.
11	Alkanolamines	U.S.P. 2,891,098-32	Coler, M. A.
12	"	U.S.P. 2,870,224	"
13	"	U.S.P. 2,922,770-73	"
14	Substituted cyclic ether	B.P. 896,798	Chemische Werke Hüls A.-G.
15	Copolymer with unsaturated acid esterified with a polyhydric alcohol	U.S.P. 2,912,113	Monsanto Chemical Co.
16	Introduction of carboxyl and acetoxy groups into the benzene rings	U.S.P. 2,945,839	Monsanto Chemical Co.

**Appendix III***Antioxidants*

No.	Type of Additive	Patent No.	Patentee
17	Phenols	U.S.P. 2,917,560	Dow Chemical Co.
18	"	B.P. 777,494	Monsanto Chemical Co.
19	"	U.S.P. 2,886,577	Ethyl Corp.
20	Amines	U.S.P. 2,789,962	Union Carbide Corp.
21	Oximes	U.S.P. 2,911,385	Dow Chemical Co.

## Appendix IV

*Light stabilisers*

No.	Type of Additive	Patent No.	Patenter
22	Sulcoylmorpholines	U.S.P. 2,906,729	Dow Chemical Co.
23	Salicylate- $\alpha$ -alkanolamine	U.S.P. 2,732,268	" " "
24	Dibenzoylresorcinols	B.P. 786,114	" " "
25	Hydroxybenzophenone ethers	B.P. 810,570	American Cyanamid Co.

## Appendix V

*Copolymers*

No.	Comonomer co-polymerized with styrene	Patent No.	Patenter
26	Acrylonitrile	B.P. 811,685	Dow Chemical Co.
27	"	Ger. P. 961,309	Badische Anilin- u. Soda-Fabrik A.-G.
28	"	Ger. P. 1,003,116	Badische Anilin- u. Soda-Fabrik A.-G.
29	Methylstyrene, acrylonitrile	U.S.P. 2,881,146	Monsanto Chemical Co.
30	Methylstyrene, acrylic acid	U.S.P. 2,816,890	" " "
31	Methylstyrene, methacrylonitrile	U.S.P. 2,851,439	" " "
32	Methylstyrene, methacrylic acid	U.S.P. 2,816,890	" " "
33	Methylstyrene, dialkyl fumarate	U.S.P. 2,856,580	" " "
34	Acrylonitrile, maleic anhydride	B.P. 816,618	Diamond Alkali Co.
35	Acrylonitrile, dialkyl fumarate	U.S.P. 2,829,128	Monsanto Chemical Co.
36	Methacrylonitrile, acrylic acid	U.S.P. 2,551,111	" " "
37	Acrylonitrile, methyl methacrylate	U.S.P. 2,815,849	" " "
38	"	U.S.P. 2,851,147	" " "
39	Acrylic acid, methyl methacrylate	U.S.P. 2,851,148	" " "
40	Acrylic acid, methyl vinyl ketone	U.S.P. 2,859,125	" " "
41	Acenaphthylene	U.S.P. 2,803,622	" " "
42	Conium	U.S.P. 2,809,187	" " "
<i>Graft</i>			
43		U.S.P. 2,882,259	Rohm & Haas Co.
44	Methacrylic acid, ethyl acrylate	B.P. 819,066	Du Pont de Nemours & Co.
45	Acrolein	U.S.P. 2,995,650	Monsanto Chemical Co.
<i>Block</i>			
46	$\beta$ -Propiolactone	U.S.P. 2,835,658	Dow Chemical Co.

## Appendix VI

*Toughened polymers and copolymers*

No.	Bound monomer(s) in base polymer	Bound monomer(s) in rubber	Patent No.	Patentee
47	Styrene	(High gel content)	B.P. 843,722	Styrene Products Ltd.
48	"	(Cross-linking SBR in blend)	B.P. 824,368	" " " "
49	"	(Cross-linking SBR)	U.S.P. 2,882,268	Dow Chemical Co. "
50	"	Ethylene	B.P. 835,576	Montecatini Soc. Gen.
51	"	Chlorosulphonated ethylene	U.S.P. 2,854,749	Monsanto Chemical Co.
52	"	Ethylene-vinylene carbonate	U.S.P. 2,945,836	" " " "
53	"	Oxidised isobutylene	U.S.P. 2,804,443	" " " "
54	"	Butadiene	B.P. 832,308	Koppers Co. Inc. "
55	"	"	B.P. 840,163	U.S. Rubber Co.
56	"	Hydrogenated butadiene	U.S.P. 2,854,750	Monsanto Chemical Co.
57	"	Butadiene-styrene	U.S.P. 2,863,849	" " " "
58	"	"	B.P. 757,631	Chemische Werke Huls A.-G.
59	"	(plus polyethylene glycol)	B.P. 821,889	Dow Chemical Co.
60	"	Butadiene-styrene-divinylbenzene	U.S.P. 2,808,386	Koppers Co. Inc.
61	"	Isoprene-methyl methacrylate	U.S.P. 2,891,018	Distillers Co. Ltd.
62	"	Dialkyl fumarate-soya bean oil	U.S.P. 2,821,846	Monsanto Chemical Co.
63	Styrene-acrylonitrile	Isobutylene	U.S.P. 2,833,746	Ethyl Corp.
64	"	Butadiene	U.S.P. 2,802,808	Firestone Tire & Rubber Co.
65	"	"	B.P. 802,094	Goodyear Tire & Rubber Co.
66	"	"	B.P. 812,808	Union Carbide Corp.
67	"	"	B.P. 844,141	U.S. Rubber Co.
68	"	Butadiene-styrene	B.P. 794,400	" " " "
69	"	"	U.S.P. 2,941,981	Dow Chemical Co.
70	"	Butadiene-acrylonitrile	B.P. 778,265	Monsanto Chemical Co.
71	"	"	B.P. 817,141	Imperial Chemical Industries Ltd.
72	"	Butadiene-acrylonitrile-acrylic acid	B.P. 857,704	Farbenfabriken-Bayer A.-G.
73	"	Butadiene-methacrylonitrile	B.P. 832,823	Imperial Chemical Industries Ltd.
74	"	Ethyl acrylate	U.S.P. 2,853,646	Goodyear Tire & Rubber Co.
75	"	Octyl acrylate-vinyl chloride	U.S.P. 2,888,308	Union Carbide Corp.
76	Styrene-methacrylonitrile	Butadiene	B.P. 832,822	Imperial Chemical Industries Ltd.
77	Styrene-methacrylic acid	Butadiene-styrene-methacrylic acid	U.S.P. 2,927,035	U.S. Rubber Co.
78	$\alpha$ -Methylstyrene-acrylonitrile	Butadiene	U.S.P. 2,908,661	Borg Warner Corp.
79	Styrene-acrylonitrile-methyl methacrylate	"	B.P. 833,002	Imperial Chemical Industries Ltd.
80	Styrene-acrylonitrile-methyl methacrylate	"	B.P. 841,215	Imperial Chemical Industries Ltd.
81	Styrene-acrylonitrile-methacrylic acid	Butadiene-acrylonitrile	B.P. 804,596	Styrene Products Ltd.

## RESINS, DRYING OILS, VARNISHES AND PAINTS

By MEMBERS OF THE OIL AND COLOUR CHEMISTS'  
ASSOCIATION

(Convenor: I. C. R. BEWS)

NATURAL AND SYNTHETIC RESINS (P. Unger)

*W. A. Mitchell & Smith Ltd., Mitcham*

INCORPORATION of different functional groups into one resin molecule continues to be increasingly practised, making classification more and more difficult. Many new raw materials have become readily available, particularly for alkyd resins, reflecting the shortage of established materials and of natural resins as well as fruition of new methods of manufacture. Among novel products described may be singled out development in polycarbonate coating resins, preparation of an unsaturated cyclic boron-containing polymer (1) and resins based on a natural product, boleko oil (2).

### Alkyds and polyesters

A method for calculating viscosities of simple alkyd resin solutions has been developed (3), based on an equation relating ideal behaviour with that found in practice. It enables the viscosity of solutions of a particular alkyd in any solvent to be calculated using a single determination in another solvent and solvents of known characteristics. Tables of experimental and calculated results are presented. The Flory theory of gelation of alkyd resins has been extended to cover mixtures of mono- and di-basic acids with pentaerythritol or two different polyols (4). Unlike the Carothers equation, the relationship obtained has given good agreement with experimental results.

Formaldehyde has been used as a functionality reducer in pentaerythritol alkyds (5) and is added at any time after the alcoholysis stage, prevents gelation in short oil formulations and reduces phthalic anhydride sublimation. Its effect is explained by cyclic formal formation, which is shown by the splitting off of water. Modification of alkyds with benzoic acid has been claimed to improve the alkali resistance (6). The fatty acid used is pre-reacted

with the benzoic acid and it is thought that this leads to cross-linking through the benzene nucleus in the final film. Alkyds modified with salicylic acid have good through-dry and heat-resisting properties (7).

New processes for making vinyl monomer modified alkyds of desired properties have been described but are largely empirical. A study of the reaction of drying oils with styrene, vinyltoluene and cyclopentadiene (8) under widely different conditions, followed by isolation and identification of the products, has illustrated the complexity of the polymerisation processes involved. Preparation of highly styrenated epoxy esters has been surveyed (9), attention being drawn to single-stage methods for making vinyl-modified polyesters.

Improved water-dispersible styrenated alkyds based on polyglycols have been claimed to give glossy pigmented films (10) and to require no colloidal stabiliser, which results in better water-resistance. Publication in the United Kingdom of a further patent describing the Hoenel finishes (11) has given examples of the hydrogen peroxide treatment of the polyester portion to improve compatibility and film properties.

There have been many new ways of preventing air-inhibition of the cure of unsaturated polyesters, including the use of an unsaturated diol (12), of epoxidised unsaturated oils (13) and the addition of stearyl esters (14) and of tung oil (15). Examples of novel catalyst and stabilising systems for unsaturated polyesters involving, among others, salts of various transition metals, have been given in the patent literature.

#### **Amine- and phenol-formaldehyde resins**

A method of preparing novel, very stable solutions of high formaldehyde content involves absorption of generated formaldehyde gas into urea or melamine (16). Examples of a process for the continuous manufacture of resins from these are given. Amino resin production and properties, with particular reference to available raw materials, have been reviewed (17). The effect of impurities, e.g., traces of aluminium, on the condensation rate of melamine with formaldehyde has been considered (18). Preparation and use of new substituted melamines, including *NN*-substituted melamines (19), cyclohexylmelamine (20), *N*-*t*-octylmelamine (21) and also melamine-formaldehyde resins etherified with but-2-en-1-ol (22) have been described. Heat-curing, water-soluble melamine-formaldehyde resins have been obtained by co-condensing melamine with aldehydes and ketones (23).

Details have been given of the use of a diphenolic acid, 4,4-bis-(1-hydroxyphenyl)pentanoic acid, for preparing a whole series of resins suitable for stoving films (24). Hoenel (11) has described

examples of water-thinned phenolic resins derived from phenolic acids.

### Epoxide resins

The detailed mechanism of the cure of epoxide resins by amines has been reviewed (25). Cured products have been examined by infra-red spectroscopy and the effect of the structure of the amine is discussed. Preparation of epoxide resins from various new sources has been reviewed (26). Direct epoxidation of unsaturated olefins and aldehydes has been achieved with hydrogen peroxide (27, 28). Continuous production of glycidyl polyethers is effected by contacting an epichlorohydrin, phenol and acetone-water feed mixture in an elongated, heated tube in the presence of alkali (29). Liquid epoxy resins have been modified by catalytic reaction with acids and phenols to give varnishes (26, 30).

### Ethenoid resins

Interest in thermosetting acrylic resins has been maintained. One series is prepared by incorporating a proportion of acrylamide into a vinyl copolymer and subsequently reacting the amide amino groups with formaldehyde, and then etherifying (31*a*). By making use of the wide compatibility with other resins and adjusting the components of the vinyl copolymer, products with tailor-made characteristics can be obtained (31*b, c*). Other systems are based on mixtures of amino or epoxy resins with acrylic copolymers containing respectively carboxyl (32, 32*a*) or hydroxyl (33*b*) groups, in order to achieve compatibility. Products of partially polymerised non-drying alkyds with vinyl copolymers containing epoxy groups for cure with amino resins have also been prepared (34).

Analogous thermosetting aqueous dispersions of acrylic copolymers mixed with glycol epoxy ethers (35) and emulsions of epoxy-acrylic-aldehyde copolymers for cold-curing with amines have been obtained (36). Other aqueous stoving systems have included cross-linked methyl vinyl ether maleic anhydride copolymers (37), mixtures of acrylic emulsions and aqueous phenol-formaldehyde resins (38) and modified polyvinyl acetate emulsion (39).

### Resin analysis

Many of the papers dealing with resin analysis published during the past 25 years have been collected and edited and are now available in one volume (40). New spot-test reagents have been utilised for resin identification (41) and a procedure for analysing chlorosulphonated polyethylene resins has been developed (42). ASTM standards for the determination of the epoxy content of resins (43*a*) and of benzoic acid and phthalic acid isomers (43*b*), as

well as of rosin (43c), in alkyds, have been issued. Any dicarboxylic acid, including isophthalic acid, in alkyd resins may be estimated by titration with alkali in a non-aqueous medium (44). Results of comprehensive alkyd analyses, including the use of paper-chromatography and ion-exchange resin techniques, have been published (45). Polyols in unsaturated polyesters have been identified by the former technique (46).

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## PIGMENTS AND PAINTS (R. J. Cole, B.Sc., F.R.I.C., A.M.I.Chem.E.)

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### Pigments

THERE would appear to be a few new pigments of some significance: a vapour-phase zinc sulphide-coated barium sulphate (e.g.,  $8^{90}_{90}$  ZnS) has been claimed to be superior to ordinary process lithopone (1), spinel-type compounds of the formula  $MO, Al_2O_3$  (where M is Mg, Zn or Ca) proposed as inexpensive chalk-resisting white pigments or fillers (2), and calcined lead phosphate/silicate claimed to reduce paint blistering (3). The influence of trace elements and the use of sodium hypochlorite as oxidising agent for the iron in ferrite yellow pigment preparations have been studied (4).

The following are among many interesting examples of pigment pretreatments and pigment/medium interaction products: insoluble cross-linked vinyl or vinyl/allyl treatment (5), vapour-phase ethylenically unsaturated monomer treatment in the presence of a free-radical generating polymerisation initiator (6), and a polymeric azo dye made by diazotising a copolymer of aminostyrene and methacrylic acid and suitably coupling (7).

An important comprehensive study of the light-fastness of organic pigments has been carried out, a large number of these pigments being used as tinters for chalk-resistant titanium dioxide in five paint systems at three concentrations. Exposures were made outdoors (Florida up to 9 months) and the colour changes reported in NBS units. Organic pigments now provide a full spectrum of hues in any degree of light-fastness, provided that a number of vat colours, specially prepared for paint purposes, are included (8).

The reinforcing properties of carbon blacks in rubber have been well studied, but for a number of years now it has become increasingly apparent that carbon blacks are not chemically inert. The concept of an acidic surface was once invoked to explain dispersion of the pigment in oleoresinous paint media (9), but recently the importance of quinone and hydroquinone groupings on carbon black surfaces, revealed by infra-red spectroscopy (10), has received emphasis, and a quantitative chemical method of determination has been described (11).

The performance of a precipitated pigment in paint making is affected by the way it is dried from the water-wet paste. Spray drying has many advantages but there have been economic difficulties. Of interest, therefore, is a new spray dryer which is claimed to be capable of drying pastes of much lower water content than was previously considered possible (12). Also, freeze drying of pigments has been claimed to give rise to easily dispersible material (13). The question of whether more water-wet pigments might not be 'flushed' directly into paint media to obviate drying altogether is a perennial subject for discussion (14); some new patented procedures have appeared (15).

Many important contributions to the knowledge of powders in general, and pigments in particular, have been made at a recent symposium (16), and fundamental problems presented by the use of different methods of particle-size analysis and the utilisation of the data obtained have been reviewed (17). Interest in rapid, accurate methods of particle-size analysis continues; a noteworthy addition being the determination of the number and size of particles suspended in an electrically conducting liquid by the change in electrical resistance which occurs on displacement of the electrolyte by particles as they pass through a small aperture (at a claimed speed of 6000 particles per sec.) (18). Krypton adsorption and gas chromatographic procedures (19) for specific surface area

have been described. Very-high-resolution electron microscopy (magnification of 10,000 to >200,000 times) is at present a comparatively unexplored field of examination for pigments, but some interesting preliminary results have been published (20, 21).

## Paints

### *Pigment dispersion*

Difficulties of definition and measurement of pigment dispersion in paints still exist (22). Bell (21) has emphasised the importance of attempting to 'see' (i.e., in the electron-microscope sense) what goes on at the pigment-medium interface and has pointed out advances in this field made in systems of biological importance (23) etc. Moll (24) points out that mixing procedures are most efficient when conditions allow maximum contribution by the pigment to its own dispersion (pigment/volume concentration, etc.), and that 'seeding', arising from dilution after milling high pigment low resin pastes, can be reduced by lowering the differential resin concentration at the dilution boundary.

Sedimentation volume as a measure of the extent of pigment dispersion has been considered by Robinson (25) and Beckmanis & Kovacs (26). Robinson follows progress in dispersion by change in the volume which the pigment effectively occupies (relative sedimentation volume) and thereby links dispersion with packing, which has been considered by many authors (27). After deflocculation or disaggregation, particles of a pigment are able to pack together more closely. The conditions under which a machine can apply force in a dispersion process to bring about the separation of pigment particles are governed by the proportionality between the volumes of the liquid phase and of the voids between the particles, the latter being directly related to sedimentation volume. It is suggested that the performance of different types of dispersion machines, particularly kneader as against high-speed agitator-type, might be compared from the solids content relative sedimentation volume plot (25).

Beckmanis & Kovacs consider measurements of sedimentation volume to be better measures of pigment dispersion than viscosity-shear rate relationships. They studied linseed oil alkyds as ball-mill grinding media for titanium dioxide and reported a definite (50% excess over stoichiometric) pentaerythritol content for such alkyds to have optimum grinding efficiency. This result is explained on the basis of the 'polar nature' and molecular weight of the medium, using a concept of Dintenfuss (28) that polar nature must be 'supported' by a molecular weight large enough to nullify van der Waals forces. It is suggested that higher pentaerythritol contents would have the effect of reducing the molecular weight, thereby

offsetting the dispersion factor, which is considered as dependent on an increased number of polar groups in the molecule.

The effect of fatty acid and molecular complexity of media in dispersion processes for whitening have been described. Fatty acids are considered to form thin, and complex media to form thick, interfacial layers (this affects oil absorption); fatty acids displace adsorbed polymeric materials from whitening surfaces (29).

Effects of paint-making procedures on the state of pigment dispersion obtained are, e.g., effect of solvent balances in an epoxy-urea system, flocculation at the 'letdown' process after mixing at high pigment loading, flocculation caused by incompatible varnishes, specific effects with a styrenated alkyd system, etc. The state of dispersion has been satisfactorily studied with the optical microscope ( $\times 450$  for titanium dioxide paints). With such a method of evaluation, application of the cover glass in the preparation of the microscope slide will often cause the appearance of complete dispersion when viewed immediately; in a flocculating system, however, this will be evident after a lapse of a certain time. By making suitable comparisons and giving time for potential flocculation to occur, the technique allows the effect of corrective measures to be examined (30).

#### *Universal tinters*

Since the last Report (27), another patented procedure has appeared (31) and Haberfeld (32) has discussed the problem as the formulation of a set of dispersions of suitable pigments in such a vehicle that both solvent-base and latex-base paints (both for architectural finishes) may be uniformly tinted. Difficulties have been experienced in the selection of suitable bright red and yellow pigments for this purpose. As far as the vehicle is concerned, a

solubility parameter  $\sim \left( \frac{\text{Heat of vaporisation} \times \text{density}}{\text{Molecular weight}} \right)^{\frac{1}{2}}$  has been

suggested and the value should be between 8.4 and 8.5 for universal tinters, but evaporation rate, miscibility with water and viscosity are also considered important (33). A high viscosity should be used so that the amount of non-volatile matter is minimum. The preferred procedure is to disperse the pigment in an oil-soluble but emulsifiable binder; for final use, predispersion in water (for latex paint) or in white spirit (for oil-bound paint) is recommended. Surface-agent selection can be made on the basis of H.L.B. number (hydrophile-lipophile balance) (34). Scheufele (35) also refers to H.L.B. and considers the selection of surface agent the most important factor in formulating universal tinters; with nonyl-phenol-ethylene oxide condensates a sharp maximum in effectiveness was found at a particular ethylene oxide content.

*Heat-resistant coatings*

McKinnie (36) has reviewed an interesting field of special coatings, described as 'ceramic frit' or 'conversion coatings'. When subjected to heat sufficient to destroy any organic binder, such materials are converted into coatings more or less similar, according to temperature conditions, to ceramic coatings. One aim of the development is to reduce the gap between organic and ceramic coatings, a demand for such coatings, e.g., for missile applications, in the U.S. being indicated by certain official specifications (37). Some of the newer refractory materials involved in these coatings are metal carbides, sulphides, nitrides and borides, whilst lead and zinc oxides are stated to increase the adhesion of the coatings to metal surfaces. In addition, 'bloating'-type coatings containing carbonates that evolve carbon dioxide on heating are said to be potentially useful for fire-resistant applications.

A new polymer, described as more like a ceramic than a plastic, has a temperature stability of 1110°F, compared with a maximum of 500°F for known organic polymers and 900°F for certain known inorganic polymers, e.g., phosphinoborines of U.S. development. The composition of this material has not yet been disclosed, but it may be related to poly-phenyleneboronous acid (38).

*General*

Questions of paint durability, corrosion protection, etc., continue to engage much attention and painting conditions overseas and methods of test used in other countries are of growing interest. The importance of surface preparation before painting continues to be emphasised (39).

Certain publications of the Paint Research Station previously held confidential to members have been released for more general circulation.

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## DRYING OILS, DRIERS AND VARNISHES (G. H.

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CHEMICAL modification of natural fats for the production of chemical intermediates, plasticisers and polymers has been a topic of major interest, and the developments in this field show promise of new outlets for unsaturated vegetable oils in the surface coating and allied industries. In the U.S.A. there has been continuing interest in vinyl ether polymers derived from drying oils and in epoxidised oils; both animal and vegetable fats have been investigated as raw materials for oleochemicals. In the United Kingdom new information has been published on the chemistry of fatty acid condensation products (unsaponifiable drying oils).

The expanding alkyd resin industry continues to find a ready market for drying oils and there have been several recent contributions on the use of tung oil and segregated fish oils in this field. (See Supplementary Bibliography.)

### Drying oils

Linseed oil has continued to be the principal drying oil and there has been an increasing interest in soya-bean oil for alkyd resin manufacture. There has been little further information as to the availability of safflower seed oil, although there are indications that there is increasing cultivation of the plant in the U.S.A. (7). An oil of the linoleic-rich class such as this would find a ready market in the paint industry if it were available in quantity and at prices competitive with those for linseed and soya-bean oils.

A new method for the polymerisation of drying oils has been investigated in Holland (2). 'Voltolisation' of linseed oil by the action of electric discharges in a low-pressure hydrogen atmosphere produces a polymerised product with a structure completely different from that of the thermally polymerised oil. In contrast with the thermal product, it has a higher degree of polymerisation at low viscosity and contains very little cyclic material. It is suggested that the polymerisation proceeds through the coupling of radicals formed by the action of atomic hydrogen. Some information on surface coating and pigment wetting properties of Voltolised oils would be useful. The effects on drying oils of  $\gamma$ -radiation from a  $^{60}\text{Co}$  source have been investigated (3). With linseed and soya-bean oils, there was a bleaching effect, increase in viscosity, and a tendency for the unsaturation to undergo structural changes (*cis trans* isomerisation and conjugation); tung oil showed a decrease in conjugation and polymerisation to a benzene-insoluble product. It has been concluded that the extensive radiation necessary to effect desirable changes would not be economically practical at this present time. For further information on irradiated oils attention may be drawn to the studies conducted some years ago at the Paint Research Station (4).

For a study of the chemical constitution of drying and semi-drying oils, gas chromatography is an important analytical tool and there have been several recent papers on the subject (5). New developments in liquid partitioning agents (5*a, b*) have made possible the complete separation of methyl esters of drying oil fatty acids; the method is accurate and ideally suitable for the rapid analysis of micro quantities of fats and oils.

The reactions of drying oils with hydrocarbon monomers (styrene, vinyltoluene, cyclopentadiene) have been investigated (6) and the nature of the reactions, the chemistry of adducts and copolymers and various methods of modification, have been studied. In the treatment of drying oils, vinyltoluene differs from styrene in that it can be incorporated with greater ease to give homogeneous polymers; in other respects the two behave similarly as vinyl monomers in the various polymerisation reactions. Cyclopentadiene, in contrast with the other two monomers, appears to



combine with the unsaturated fatty chains via formation of highly reactive Diels-Alder adducts.

### New products from drying oils and fatty acids

There has been a sustained interest in vinyl ether polymers derived from linseed and soya-bean fatty alcohols, and the trend towards their commercial development has been maintained. Mustakas *et al.* (7a) investigated processing conditions in the atmospheric vinylation of conjugated soya-bean alcohol, using welding-grade acetylene gas and potassium hydroxide catalyst, the highest yield being obtained with 4% KOH at 180-190°. In the polymerisation of vinyl ether monomers variables such as catalyst concentration ( $\text{SnCl}_4$ ), initiation temperature, type of solvent and influence of moisture, etc., have been studied (7b). A process has been developed (7c) for the pilot-plant preparation of conjugated soya-bean-lower alkyl vinyl ether copolymers and further progress towards commercial production is indicated by the development of methods for catalyst disposal and solvent recovery. Gast *et al.* (7d) have prepared the non-conjugated vinyl ether monomers from linseed oil alcohols by trans-etherification with ethyl vinyl ether and studied the film-forming properties (air drying and stoving) of the non-conjugated homopolymers and copolymers. Stoved films had excellent adhesion to glass, black iron and aluminium substrates and were unusually resistant to chemical attack. Another interesting development in this field (8) concerns the copolymerisation of polyunsaturated vinyl ethers with polyreactive monomers, e.g., allyl vinyl ether and 1,2-divinyloxyethane. On subsequent polymerisation and film formation the cross-linking action of such monomers would be expected to lead to increased film hardness and chemical resistance.

Applications for fatty acid derivatives in the field of epoxy resins have been described by Gelb and co-workers (9a). Epoxy resins have been made from epoxidised glyceride oils and phthalic anhydride in the presence of an amine accelerator and various other epoxy resin systems incorporating epoxidised soya-bean oil have been investigated (9b, 10).

Developments in 'oleochemicals' have been discussed by Ault (11), and there appear to be new industrial outlets for animal and vegetable fats. Interesting new materials having potential value as plasticisers are the fatty derivatives containing a phosphorus-to-carbon bond, e.g., trialkyl 9,10-phosphonostearates.

There has been fresh information on unsaponifiable condensation products (12). These novel materials are drying oils obtained by heating unsaturated fatty acids under certain conditions in the presence of boric acid. The mechanism of the condensation reaction has been studied, the evidence supporting the view that the main products are pyrones formed by the condensation of four molecules

of fatty acid with decomposition of their carboxyl groups. It is probable that the intermediate compounds are ketones and anhydrides, which form a boron complex with the catalyst. This decomposes on further heating to produce pyrones. There is also information on the preparation and properties of varnishes based on condensation products and a variety of resins. Polymerisation and condensation reactions of fatty acid derivatives have been studied by Clément (13) and Poisson (14).  $\beta$ -Keto-esters from the Claisen condensation of ethyl esters of drying oil fatty acids have film-forming properties, as have their products of saponification (symmetrical ketones) (13); ethyl esters of drying oil fatty acids can be condensed with linseed oil to form a  $\beta$ -keto-triester of enhanced reactivity. Polyketo-diacids from the Claisen condensation of diethyl sebacate have also been obtained. Poisson (14) has studied a new class of monoamides and polyamides derived from drying oil fatty acids. The former are prepared by the condensation of unsaturated fatty acid with the corresponding amine, and diamides from a polyamine such as hexamethylenediamine and an unsaturated fatty acid. The thermal polymerisation and autoxidation of these compounds leads to the formation of chemically resistant products.

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**CELLULOSE ESTER AND ETHER VARNISHES (E. H. Davies)**

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**Coatings**

THE stabilisation of cellulose ester or ether films against ultra-violet degradation is achieved by incorporation of a polymer of vinyl or allyl salicylate in the lacquer (1) and (specifically for ethyl cellulose films) 2,4-dihydroxybenzophenone. The addition of 1% by weight (calculated on the ethyl cellulose content) is necessary, but an antioxidant, *p*-*t*-pentylphenol, is ineffective even at 5% concentration. Mixtures of this antioxidant and the ultra-violet absorber (0.5% each) are, however, effective (2). The prevention of atmospheric breakdown of ethyl cellulose films may be achieved by addition of 0.005-5% by weight of an antioxidant and an acid-accepting epoxy compound and 0.1-2% of a neutral organic phosphite. The preferred antioxidant is 4,4'-thiobis-(3-methyl-6-*t*-butyl)phenol (3).

The essential properties of lacquers (first and second) for application to polystyrene, cellulose acetate and other plastics employed in processes necessitating the vacuum deposition of either silver or aluminium, have been determined (4). The process of silver-spraying similar plastics depends for its success on the lacquers employed. The first lacquer should not attack the substrate and the second lacquer should not attack the first. Aliphatic solutions of acrylic or methacrylic resins as the first lacquer followed by alcoholic solutions (e.g., of polyvinyl alcohol, nitrocellulose) fulfil these conditions (5).

The adhesion of cellulose ester resin and cellulose ether/resin

lacquers to plastics has been critically examined by Thinius (6) with a view to assessing those best suited for any specific material.

A preparation containing 5-30% of cellulose acetate-butyrate (butyral content 46-50%), 5-75% of ethyl acetate, 5-75% of isobutyl acetate, 5-40% of ethyl alcohol, 5-75% of toluene and 5-35% of dimethylformamide dries rapidly and possesses excellent adhesion for vinyl copolymer plastics (7). Cellulose acetate-butyrate possesses outstanding characteristics in lacquers intended for use on insulated magnetic wire (8), and gives an excellent strippable protecting coating when combined with 8-18% of plasticiser and 0.2-1.5% of soya-bean lecithin (9).

Lacquers which remain completely tackfree are produced by combining cellulose acetate-butyrate with polymerisable styrene and other monomers (10). Completely insoluble films may be obtained from lacquers containing cellulose acetate-butyrate in conjunction with a butylated urea-formaldehyde resin. Degree of insolubility increases with increasing hydroxyl content of the acetate-butyrate, suggesting that cross-linking occurs between these groups and the urea resin. Catalysts such as butyl phosphate accelerate the reaction even at room temperature (11).

Magnetic recording tape, made from cellulose acetate, stretched to a yield point within 5% of its tensile strength, is effectively coated with a ferromagnetic composition comprising magnetic iron oxide 65%, alcohol-soluble nitrocellulose 10%, polyvinyl acetal 20% and plasticiser 5%, all dispersed in a suitable organic solvent mixture (12). For coating self-healing condensers it is advisable to use ethyl cellulose, cellulose acetate or other cellulose derivatives which do not yield oxygen on decomposition (13).

Lacquers with good stability at 28° and 98% relative humidity have been prepared from combinations of nitrocellulose and oxyterpene resins (turpentine-oxygen adduct); these lacquers also exhibit excellent resistance to mould growth under similar conditions of test (14). Furniture lacquers based on the same ingredients, with addition of oxyterpene solvent, were successful in a Russian factory, so that lacquers with high solids content could be used with hot-spray application, thereby reducing production costs by as much as 33% (15).

The adhesion of nitrocellulose lacquers to casein coatings, e.g. as used for bottom coatings on leather, is enhanced by the addition of formamide to the lacquer (16). Improvements in the adhesion, gloss and close grainedness of nitrocellulose lacquers for leather results when the lacquer is applied over a bottoming coat prepared from an aqueous emulsion of a film-forming polymer or copolymer containing a cation-active dispersive agent based on quaternary ammonium compounds, e.g., *N*-octadecyl-*N*-methylhexamethylenammonium methyl sulphate (17). The adhesion and light fastness of nitrocellulose lacquers applied to tinplate or aluminium

are improved by application of two coats of conventional lacquer, containing 1% of diphenylamine, to the metal: the coating is air-dried at room temperature and then exposed to irradiation from a quartz lamp for 20–30 min. The coatings acquire a pleasant golden colour and exhibit greatly enhanced mechanical properties (18).

The increasing use of diester lubricants by the aircraft industry has shown that conventional lacquer finishes are generally non-resistant to these lubricants. Coatings based on nitrocellulose combined with copolymers of methyl methacrylate and other acrylic esters display remarkable resistance to diester lubricants and also to abrasion and weathering (19). Similarly improved film characteristics are claimed for lacquers based on nitrocellulose and copolymers of the type butyl methacrylate/alkyd, which also permit the easy dispersion of pigments for colouring (20). Nitrocellulose lacquers containing non-drying alkyd, vinyl chloride/vinyl acetate copolymer and petroleum hydrocarbon wax have been successfully employed for the rapid de-icing of naval aircraft (21).

The electrostatic spraying of nitrocellulose lacquers reformulated with higher boiling solvents on to wood and the critical moisture of the wood itself have been examined (22). The suitability of this method of application was assessed by measuring the electrical resistance of the lacquer, this being adjusted to a suitable level by variation of the content of polar solvent. Bechtold (23) has discussed the same subject and examined the commercial processes available in this field; in his view a surface moisture content of 10% is necessary for satisfactory deposition and adhesion.

The rapid dispersion of pigments into nitrocellulose lacquers is effected by the incorporation of either *N*-vinyl- or *N*-methyl-2-pyrrolidone as a wetting and dispersing agent. Details of the correct agent to be used for a wide range of pigments are given (24).

### Analysis and testing

Nitrocellulose saponified with aqueous alkali in the presence of an organic solvent yields sufficient cellulose di- and tri-nitrate for colorimetric measurement (25) by either a spectrophotometer or a photometer. The effect of the organic solvent was investigated. In mixtures of cellulose derivatives, quantitative estimation of nitrocellulose is rapid by an infra-red technique utilising the characteristic  $11.92\ \mu$  absorption band, the error being 0.4–1.0% (26). Ion exchange has been used for qualitative identification of individual members in mixtures of cellulose ethers and esters. The procedure involves hydrolysis of the cellulose derivative, treatment with a suitable ion-exchange resin and identification of the acid component liberated. This method is also useful for mixtures of polyvinyl esters (27).

Marx-Fingi (28) has improved the accuracy of the determination of the molecular weight distribution of nitrocellulose employing

precipitation fractionation. An adsorption procedure with activated carbon is useful with limitations for the same purpose for cellulose acetate dissolved in acetone. Careful manipulation to separate the various fractions is necessary and the ratio of carbon to acetate is somewhat critical (29).

The acetic acid content of cellulose acetate has been the subject for a group study. The method comprised controlled solution in acetone/water, controlled saponification with NaOH followed by neutralisation with sulphuric acid to phenolphthalein indicator. Some interesting comparisons were revealed in the results obtained by the nine different laboratories engaged on the project (30). Lacquers intended for keeping as samples as colour standards often exhibit change both on storage and on exposure. Tests made on lacquers pigmented with titanium dioxide, a light-fast organic red, and chromium oxide alone and reduced, revealed that the most satisfactory stability could be achieved with a blend of nitro-cellulose and a coconut oil alkyd (31).

Dynamometer tests on films of cellulose acetate plasticised with dibutyl phthalate and deposited from methyl chloride/methyl alcohol solution by a controlled method, revealed that there is a significant improvement in tensile strength when the films were heated to 140–180° for 15 min. It is suggested that reorientation of the cellulose molecules produces a relaxation of stresses and an increase in molecular packing density (32). An unfractionated sample of cellulose triacetate dispersed in ethylene chlorohydrin showed greater stability on prolonged storage at 40° than did fractionated samples of the same material kept under identical conditions. The greater the degree of polymerisation of the triacetate the less stable was its solution under such test conditions (33).

The effect of prolonged heating at 160°F on nitrocellulose films has been investigated. More than forty additives were examined for their ability to confer heat stability, by measurement of the viscosity of the redissolved test films. *o*- and *p*-Methoxyphenol were the most promising (34). The stability of benzyl cellulose kept at 160°F depends upon the degree of polymerisation, unfractionated material being the least stable and those fractions of the highest and lowest degree of polymerisation exhibiting less stability than intermediate fractions. The general trend is for increased heat stability in the lower molecular fractions (35).

#### *Plasticisers*

Treating furfuraldehyde with either propionic or butyric anhydride yielded furylmethacrylic and furylethacrylic acids respectively, which on subsequent esterification, hydrogenation and ring fission produce  $\gamma$ -ketopimelic acids. These may be copolymerised to give plasticisers suitable for cellulose nitrate and cellulose acetate

(36). Isomeric acids prepared from dearomatised naphthas (boiling range 200–300°) of 55% isoparaffinic hydrocarbon content give mixtures of  $C_6$ – $C_{18}$  acids on oxidation. Esterification of these acids with glycols at 200–220° yielded esters with a higher molecular weight, lower melting point and a lower volatility than dibutyl phthalate, which makes them suitable for use as plasticisers for cellulose derivatives (37). The glycol esters of petroleum naphthenic fractions may be used similarly as plasticisers for nitrocellulose, the properties of the resultant films from such mixtures being superior to those of films prepared with castor oil derivatives (38). The acetoacetic acid esters of castor oil have also been suggested as plasticisers for nitrocellulose (39).

The reaction products of acetoacetic acid and  $C_{18}$ – $C_8$  alcohols have been examined as possible plasticisers for cellulose esters and ethers: the derivatives from butylene glycol and diglycols all exhibited good compatibility and satisfactory plasticising ability with cellulose acetate (40). Hydroxylated phosphate esters are useful for imparting flame resistance to cellulose ester or ether films (41) whilst the acetals or ketals of hydroxycarboxylic esters impart outstanding resistance to cold checking and ultra-violet light degradation (42). The manufacture of both types of ester necessitates careful control.

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## SOLVENTS (E. H. Davies)

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A WIDE range of polyols has been used industrially for many years but the increasing types of applications necessitated additions to the range. The following new polyols became available: 2-methyl-3-ethylpropane-1,2-diol; 2,2-dimethylpropane-1,3-diol; 2,2,4-trimethylpentane-1,3-diol and 2,2-dimethylbutane-1,3-diol. Their properties, uses and limitations have been described (1).

## Analysis and testing

'Solvent' and 'solvent power' are discussed by Papkov (2), who considers these properties from the standpoint of phase equilibria. A 'solvent' is defined as a liquid which, in a given temperature range, forms a one-phase, thermodynamically stable sol with a given polymer for any quantitative ratio of the components. The concept of 'solvent power' is thought to be an arbitrary phenomenon. A suitable solvent mixture for cellulose triacetate is put forward by Thummler (3), who recommends a mixture of chlorofluorinated hydrocarbons (b.p. <50°) with small amounts of chloroalkanols.

A critical examination of the dilution ratio for various liquids employed in sols of cellulose triacetate reveals that ketones generally exhibit the least precipitation effect with sols prepared by dispersion of the cellulose triacetate in various chlorinated and fluorinated alcohols blended with methanol. The precipitation effect decreases with increasing hydroxyl content of the triacetate (4).

Dintenfass (5) has investigated the problems encountered in solvating a limited number of polymers in a wide range of solvents and makes special reference to (a) effective dipole moments and its effect on the reaction between solvent and polymer, (b) dilution ratios and their relation to the fraction with low molecular weight of the tested polymer, (c) mixed and straight aniline cloud points and their relation to the molecular weight of the test solvent. A new method for determining thiophen in hydrocarbons is outlined (6) and improved test methods for measuring the hydrocarbon content of lacquer and paint thinner put forward (7). A colorimetric process of solvent identification is based on the colours resulting when mixed solvents are mixed with an equal volume of concentrated sulphuric acid (8).

Measurement of the evaporation rate of mixed solvents by means of the thin film evaporimeter is improved by the inclusion of an automatic recording balance in the apparatus (9). Mixtures of methanol with methyl acetate may be separated by adding water to the mixture, extracting with methylene chloride, which forms an azeotropic mixture, then distilling the non-aqueous methyl acetate-containing fraction, yielding pure methyl acetate. Methyl alcohol is recovered from the low-b.p. azeotrope by further distillation (10).

The solubility of water in hydrocarbons has been investigated by a tracer method. Dry air is saturated with tritium-labelled water and is then allowed to come into contact with the solvent under test until equilibrium is reached. Direct scintillation counting determines quantitatively the concentration of water taken up. The temperature at which the test was conducted was important (11). The solubility of lacquer solvents in water has also been examined with use of a specially designed burette. The method is rapid and accurate and affords a means of approximate determination of the volume ratio of the components in binary mixtures (12).

The dilution ratio of nitrocellulose sols for toluene is a maximum with a water concentration in the sol of less than 0.1%, above which the dilution ratio decreases rapidly. Addition of alcohols to the test sol considerably increases the water tolerance and the maximum effect is exerted by adding 20–50% of alcohol, ethyl alcohol being more effective than isopropyl or n-butyl alcohols, with s-butyl alcohol least effective (13).

Examination of sols of rubber in hydrocarbons showed that the solvent takes part in the development of a radical-chain mechanism of rubber oxidation; the more labile the hydrogen atom in the solvent molecule, the easier is the chain propagation reaction and the greater the rate of oxidation. This increased in the order: benzol, toluene, xylene, ethylbenzene, isopropylbenzene, tetralin. Analysis revealed that benzol added hydroxyl radicals during the oxidation process and liberated phenol (14).

### General

The addition of small amounts of normal aliphatic alcohols of 1-9C to blown synthetic oils based on butadiene copolymers exerts an unusual viscosity stabilisation effect. As an example an 80/20 butadiene/styrene copolymer was oxidised by blowing to improve its film-forming characteristics and then kept at a stable viscosity by the addition of 9.7-12.8% butanol (15). The flow, blush resistance and drying time of nitrocellulose lacquers were modified by adding small quantities of high-boiling solvents. The effect on any one of these properties exerted by each of two solvents, normally regarded as having similar high boiling points, was surprisingly different. It is suggested that the relative evaporation rates of high-boiling solvents are a better guide to their effectiveness than are their boiling points (16). A new solvent for use in lacquers with b.p. 223-363° consists of a mixture of alcohols, ethers and esters prepared by hydrogenation of the carbonylation product of di-isobutene (17).

High-boiling aromatic solvents used in lacquers, etc., consist mainly of trimethylbenzene combined with traces of methylethylbenzene isomers. Their solvent power for a wide range of lacquer ingredients together with their usefulness in formulating have been critically examined (18). 2-Nitropropane is suggested as a medium-boiling solvent for lacquer manufacture since its evaporation rate from deposited films is much slower than that of methyl isobutyl ketone. It permits much higher solids content in lacquers without film defects and also assists in pigment dispersion (19). Coatings intended for application to the inside of storage tanks as protection against corrosion of subsequent contents offer risk of solvent flash during application and drying; this may be overcome by inclusion of traces of halogenated solvents and particularly those which contain a substantial amount of fluorine in the molecule (20).

Trichloroethylene employed as a paint thinner is suitable in systems of finishing which embrace trichloroethylene degreasing. Such paints eliminate the need for expensive firefighting equipment, reduce production time, coating costs and factory area needed for finishing (21). A further improvement involves a trichloroethylene-based phosphatising bath (22). Improved efficiency for trichloroethylene metal degreasing is achieved when 0.5-20% of 2-methoxy-, 2-ethoxy- or 2-butoxy-ethanol or diethylene glycol monobutyl ether is added to the trichloroethylene before vaporisation (23a). A mixture of 90 parts by volume trichloroethylene and 10 parts 2-methoxyethanol is said to degrease metals completely in as little as 2½ minutes (23b).

Trichloroethylene stabilised with 0.02% of aniline and also with pure methanol were each investigated as solvents for recovering valuable gases containing waste styrene monomer. The solubility

of the gas in these solvents follows Henry's law as far as trichloroethylene is concerned, but with methanol deviations are apparent (24).

A non-flammable paint stripper, capable of removing oil, cellulose, alkyd or polyvinyl coatings, has been patented (25).

### Hazards

Organic liquids with low electrical conductivity are thought to allow the build-up of static electricity during rapid movement, e.g., pumping, leading to flashing of the mass. The following classification of the degree of flammability has been given: (a) highly flammable, flash point below 73°F, (b) flammable, flash point 73–150°F, (c) combustible, flash point above 150°F (26).

Friedrich (27) has investigated the efficiency of various halogenated hydrocarbons as fire extinguishers for lacquer fires, etc. All the solvents examined were better than water, but those containing combined iodine and bromochloromethane were considered particularly outstanding in their efficacy.

The toxic effects of solvents have received further attention. Oettel (28) has compared the differences in recommended safe concentrations laid down by the U.S.A., Germany and Russia, and West (29) has investigated the maximum safe concentrations (p.p.m.) allowable for a wide range of lacquer solvents. Ethylene glycol monomethyl ether gave rise to vomiting and other unpleasant symptoms when workers were exposed continuously to its vapour. Substitution of ethylene glycol monoethyl ether completely eliminated the trouble (30).

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## **AGRICULTURE AND FOOD**



## AGRICULTURE

By MEMBERS OF THE AGRICULTURE GROUP

(Convenor: A. G. POLLARD,  
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SOILS (A. H. Cornfield, M.Sc., Ph.D., A.R.C.S., F.R.I.C.)

### Organic matter

The decomposition products of the leaf litter under forest trees are of obvious importance in the nutrition of the trees, particularly where no fertilisers are applied. Ivarson & Sowden (1) compared the decomposition, during incubation in the laboratory, of the litter from a brown forest soil (mildly acid) under deciduous trees with that from a podzol (strongly acid) under coniferous trees. Losses of dry matter during incubation were greater from the deciduous than from the coniferous litter and the extent of formation of ammonia from organic nitrogenous material was also greater from the deciduous litter. Nitrate was formed only during the later stages of incubation and then only in the deciduous litter. Changes in the total as well as in the individual amino-acids in litter hydrolysates are also reported. The total amino-acids as a percentage of the total nitrogen first increased and then decreased, the rate of decrease being greater with the deciduous than with the coniferous litter. There were, however, no significant differences in the pattern of changes of the individual amino-acids between the two types of litter. Bocock *et al.* (2) and Gilbert & Bocock (3) studied the *in situ* decomposition of samples of oak and ash litter on brown forest soils, one being a mildly acid mull type overlying limestone and the other a strongly acid mor or moder type overlying slate. Losses of dry matter in oak litter occurred at the same rate from both sites over 14 months. The losses of ash litter were greater than those of oak litter at both sites, the rate of loss being greater on the mull than on the moder. On the mull much of the disappearance of organic matter was thought to be due to the activity of earthworms. The nitrogen content of the litter increased with time in both ash and oak litters on moder, but remained constant or increased only slightly in the ash and oak litters on mull.

A fundamental study of organic matter is reported by Drobnik (4), who determined the respiration rate in the Warburg apparatus



of soils treated with glucose. During the initial, primary oxidation, stage the respiration rate increased to a maximum until all the glucose had decomposed. Thereafter, in the secondary oxidation stage, the respiration rate declined. The primary oxidation is due initially to the enzyme activity present originally in the soil and later to microbially synthesised enzymes. A method of assessing the proportion of the two components involved in the primary oxidation is described.

Studies of the nature of the organic substances present in humus are as yet limited by the lack of suitable methods for extracting humus from soil in an unchanged form as well as for separating the large number of complex compounds present in humus. Coulson *et al.* (5) studied paper and column chromatography, under partition and ion-exchange conditions, high- and low-voltage paper electrophoresis and gelatin-gel diffusion methods for fractionating humic acids. Only limited success was obtained and the results confirmed the very complex nature of the humus system. Schwartz (6) separated from soils, by chromatographic techniques, acetic and formic acid, small amounts of lactic and succinic acids and traces of isocitric and tartaric acids. On aerobic incubation of soils, alone or mixed with lucerne, acetic and formic acids predominated initially but isocitric and tartaric acids increased later. This indicates the importance of microbiological activity in altering the organic acid balance in soils and thus affecting the availability of soil nutrients. In this study the increase in isocitric and tartaric acids was accompanied by an increase in 'available' phosphorus as measured by extraction with 0.5M-sodium bicarbonate.

Differential thermal analysis has long been used for identifying minerals and clays in mixtures, but recently Chesters *et al.* (7) have suggested the possibility of applying the method to the soil organic fraction. They present thermograms of 38 organic acids and their derivatives over the temperature range 50–800°. Reproducibility of the thermograms was good and they readily distinguished between the different materials even when these were quite closely related.

Many extraction techniques have been described for separating the organic from the mineral fraction of soils. These methods suffered from the drawback that they either extract only a small proportion of the total organic matter present or yield the organic matter in a form which is different from that originally in the soil. Anhydrous formic acid, particularly when hot, is an effective extractant of organic matter from both soils and composts (8). The efficiency of extraction was increased by inorganic cations and the dissolved material was recovered by precipitation with di-isopropyl ether containing 1% of acetyl chloride, which held inorganic cations in solution. The recovered organic material had a good physical condition and was low in ash. The carbon/nitrogen ratio and the pattern of sugars, uronic acids, and amino-acids obtained

on hydrolysis of the extracted material did not differ markedly from that remaining in the soil residue. The method was fairly efficient in extracting organic matter, in that 27-43% of the organically bound nitrogen in soils and 62-87% of that in composts was removed.

### Nitrogen

Birch (9), working with African soils, found that the extent of mineralisation of carbon and nitrogen during a standard incubation period increased with the length of the period during which the soils had been in air-dried storage prior to incubation. These results are similar to those obtained by Harpstead & Brage (10) working with American soils, although the latter workers determined only nitrate. These findings raise a number of interesting implications. There are many advantages in using air-dried over field-moist soils during laboratory studies. Since it appears, however, that chemical and/or biological changes may occur in air-dried soils during storage, the period of storage may well have important effects on the results. This may apply not only to carbon and nitrogen, but also to phosphorus, sulphur and other nutrients which are intimately associated with the organic fraction of soils. Another interesting implication of these findings lies in the extent to which the drying-out of soils in the field may influence the extent of mineralisation, and hence availability, of nitrogen when the soils are re-wetted. This applies in particular to tropical soils which are subject to well-defined wet and dry periods. Here the fertiliser equivalent of the extra nitrogen which is mineralised as a result of the soil being in a dried condition for a certain period may be considerable. Birch has estimated that this may amount to over a ton of ammonium sulphate per acre due to a 15-week 'dry' period for a soil high in humus, and 300 lb. per acre even for a soil of low humus content. He has also discussed at considerable length the implications of his results on nitrogen fertiliser trials, irrigation, effect of shade plants and other factors.

The increasing extent to which nitrogenous fertilisers are being applied to soils in the United States in the autumn has led to further studies on the effects of low temperatures on nitrification. Anderson (11) found that nitrate production in a sandy loam treated with anhydrous ammonia (150 p.p.m.) was low at 2.7° but increased with temperature up to 11.1°. Nitrate accumulation during 12 weeks expressed as a percentage of that occurring at 11.1° was 72, 35, and 4 at 8.3°, 5.6°, and 2.7° respectively. Sabey *et al.* (12) found that during incubation of soils treated with ammonium salts the plot of nitrate formed against time gave a sigmoid curve indicating an initial delay phase followed by a maximum nitrate-producing phase followed by a decline in rate of

nitrate production. There were considerable variations in both the delay phase and the maximum nitrate-producing phase between different soils. The former increased and the latter decreased with increasing temperature of incubation from 0° to 25°. Eno (13) has described an interesting method for studying nitrification of ammonia in the field. A sample of the soil is enclosed in a polythene bag which is then buried in the soil and sampled at appropriate intervals for analysis. Polythene is permeable to both oxygen and carbon dioxide, has a low permeability to water vapour and does not lead to loss of nitrate by diffusion. The method is particularly useful where the complicating factor of leaching-out of nitrate by rainfall is to be avoided. The use of black polyethylene film as surface mulches for reducing weeds and conserving moisture in row-cropped soils has been shown (14) to reduce movement and leaching of nitrate and also to increase the utilisation of applied nitrogen by maize.

It has now been established that losses of nitrogen may occur even from non-waterlogged soils following treatment with inorganic nitrogenous fertilisers. Clark *et al.* (15) reported on the extent of losses as related to type of nitrogenous material applied. In incubation tests with 41 arable soils treated with urea, nitrogen losses (i.e., nitrogen not recovered as ammonia, nitrite or nitrate) ranged from 2% to 40% of the nitrogen applied. Losses were usually the highest in poorly buffered soils, those which were initially acid or developed acidity during incubation and those which showed incomplete nitrification of ammonia. On the other hand, none of the soils lost nitrogen when incubated with added nitrate. Incubation with added nitrite also showed losses of nitrogen, the extent of loss increasing with decreasing soil pH. The results indicate that loss of nitrogen from aerobic soils does not occur by enzymic denitrification of nitrate, but probably by decomposition of nitrite to nitric oxide or by the reaction between nitrite and amino-acids or ammonia to give nitrogen. Allison *et al.* (16), following studies of the effect of partial pressure of oxygen on nitrogen losses from nitrate-treated soils, also concluded that there was little danger of denitrification losses from normal well-drained soils. However, in fine-textured soils after heavy rainfall denitrification may occur, particularly in poorly drained pockets because of the slow rate of oxygen diffusion. The loss would be accentuated by the presence of easily decomposable materials such as crop and root residues.

Further evidence for the presence of fixed, i.e., non-exchangeable, ammonium in soils, continues to be presented. Walsh & Murdock (17) found that all the soils examined by them contained fixed ammonium. Under moist conditions most soils fixed small amounts of applied ammonium. Freezing the soils increased the extent of fixation, but the greatest fixation was induced when the soils were

dried following addition of ammonium. The presence of fixed ammonium in certain rocks has been reported by Stevenson (18). He found that 52-68% of the total nitrogen in shales and 24-56% of that in granites was present as fixed ammonium. The implications of the existence of this reservoir of nitrogen in rocks is discussed.

Further reports on methods of assessing the nitrogen-supplying power of soils have appeared. For example, Peterson *et al.* (19) showed that the uptake of nitrogen by tobacco grown on 37 Gray-Brown Podzolic and Prairie soils in pot tests was highly correlated with both initial soil nitrate and with a microbiological test using *Aspergillus niger* for the first, but not for the second, crop. With the second crop total nitrogen uptake was significantly correlated with total soil nitrogen and organic matter, soil nitrification rate, and ammonia extracted or released by alkaline permanganate and sulphuric acid ranging from 0.1N to 18N.

### Phosphorus

Lack of space permits discussion of only a few papers on soil phosphorus which have appeared recently.

Lindsay & Moreno (20) have presented on a single solubility diagram activity isotherms of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  (variscite),  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  (strengite),  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  (fluorapatite),  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (hydroxyapatite),  $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  in which a function of the phosphate activity in solution is plotted against pH. The relative stability of these compounds in soil and changes expected to occur upon fertilising and liming may be predicted from the graph. It is assumed that the aluminium, iron and fluorine activities were limited by the solubility of gibbsite, goethite and fluorite respectively. Equations and graphs are presented for modifying the basic diagram so as to correspond with any aluminium, iron, fluorine or calcium activity found in soils or established during soil extraction.

Arambarri & Talibudeen (21) have reported on factors influencing the isotopically exchangeable phosphate in soils. In the presence of low concentration of citrate, total labile phosphate was increased in a non-calcareous and decreased in a calcareous soil. In the presence of a non-chelating ion (diethylbarbiturate) total labile phosphate decreased in both soils. The organic anions greatly decreased the 'slowly exchanging' fraction in both soils. The citrate ion usually increased the 'rapid' and 'medium' exchanging fractions, whilst the barbiturate ion either had no effect on, or decreased, them. Total labile phosphate in six out of seven soils was 8-40% higher in sodium- than in calcium-saturated soil. A much larger part of the total labile phosphate was found in solution in the sodium-saturated soils. At 25° the rate of isotopic exchange

of the more slowly exchanging forms of phosphate was four times greater in sodium- than in calcium-saturated soil, although the total labile phosphate in the two forms was similar. Increasing the temperature to 35° doubled the rate of exchange in the sodium-, but not in the calcium-, saturated soils.

Mack (22) studied the influence of soil temperature and moisture level on phosphorus availability. Increasing soil moisture from 30% to 100% of field capacity increased phosphorus uptake at high, but not at low, soil temperature. Leaching the soil decreased acid-soluble phosphorus and the aluminium phosphate fraction, but increased the alkali-soluble (ferric phosphate) fraction. Moisture present in excess of field capacity under partial anaerobic and non-leaching conditions increased acid-soluble phosphorus but decreased the amount available to plants. Losses of phosphorus by leaching were increased following freezing of the soil.

Walker *et al.* (23) investigated changes occurring in volcanic ash soil after 25 years in pasture. The soil contained more than twice as much total phosphorus as compared with its original phosphorus content under scrub. Although initially 90% of the total phosphorus was in organic combination, at the end of the period under pasture only 55% of the total phosphorus was in this form.

### Trace elements

Alban & Kubota (24) reported on the extractable cobalt of soils of the South-eastern United States in relation to the cobalt content of the leaves of black gum, *Nyssa sylvatica*. This plant is widely spread in the area and has previously been shown to be a useful indicator of the cobalt status of native forage species. The cobalt extracted from the A<sub>1</sub> horizon with 2.5% acetic acid-dithizone was highly correlated with that contained in the leaves of black gum for both the poorly-drained and well-drained soils of the region. On an average less cobalt was extracted from the former type of soils.

Hammes & Berger (25) found that the uptake in manganese by oats in pot tests with 20 soils was most highly correlated with soil manganese extracted by 0.1N-phosphoric acid from moist soils. However, results obtained by extraction with 0.2% hydroquinone, 0.1N-phosphoric acid and 1.5M-ammonium dihydrogen phosphate of air-dried soils were also significantly correlated with manganese uptake by oats. Air-dried storage prior to cropping usually increased the uptake of manganese by oats. Fractionation of the manganese of both moist and air-dried soils indicated that the extra manganese rendered available upon air-drying stemmed from the organic fraction of soil manganese.

Biggar & Fireman (26) found that the Langmuir adsorption equation described the adsorption of borate from solution by three

out of four soils. Wetting and drying the soil following the addition of water containing borate increased the maximum adsorption capacity and bonding energy of the soil for boron. Leaching experiments showed that boron was removed from three of the soils by desorption, whilst the fourth soil showed release characteristics similar to those obtained from a saturated solution of a boron compound.

### Analysis

Jeffries & Thomas (27) have described the use of extracting solutions containing long-chain polymers (Superfloc 16 or Aerofloc 3171) which assists the settlement of the soil colloids after shaking, so that the supernatant liquid may be sampled for analysis and filtration is avoided. Values for available phosphorus and potassium obtained in this way correlated highly with those obtained by conventional extraction methods using filtration.

Scott and his colleagues (28) have shown that the addition of sodium tetraphenylboron to salt solutions used for extracting micaceous minerals and soils greatly increased the efficiency of extraction of potassium, presumably by eliminating the blocking effect of the extracted potassium. The method should be particularly useful for determining the less easily available forms of potassium in the micaceous minerals.

Paul & Schmidt (29) found that both 0.1N-barium hydroxide and 0.5N-ammonium acetate (pH 6.8) were very effective in extracting free amino-acids from soils. Although the former extractant was the more efficient in recovering known amounts of amino-acid added to soils, the possibility of hydrolysis of proteins due to its high alkalinity cannot be excluded. Both solvents extracted amounts of amino-acids considerably greater than those reported for ethyl alcohol extraction, which method has been commonly used in the past.

Bardsley & Lancaster (30) have described methods for determining both the sulphate and the 'reserve' sulphur content of soils. Total sulphur is first determined by fusion with sodium bicarbonate at 500°, followed by extraction of the sulphate formed and its turbidimetric determination as barium sulphate. Soil sulphate is extracted with 0.5N-ammonium acetate-0.25N-acetic acid and also determined turbidimetrically. 'Reserve' sulphur is the difference between total sulphur and sulphate-sulphur. The uptake of sulphur by white clover in greenhouse tests with 17 soils was significantly correlated with soil 'reserve'-sulphur and not with sulphate. Another chemical method for assessing soil sulphur status is that of Kilmer & Neapass (31), who extracted the soil with 0.5M-sodium bicarbonate (pH 8.5) and determined total sulphur in the extract by the Johnson-Nishita procedure (32). For 30 surface soils there

was a high correlation between soil sulphur extracted by this method and sulphur uptake by plants in greenhouse tests.

The solvent system acetone-ethyl acetate-6N-hydrochloric acid is satisfactory for paper chromatographic separation of copper, cobalt, nickel and zinc in 0.5N-acetic acid and 0.1N-hydrochloric acid extracts of soils (33). After treatment of the paper with rubeanic acid spray the copper, cobalt and nickel spots are determined quantitatively with an automatic-recording reflectance densitometer. Where low concentrations of cobalt were present 1-nitroso-2-naphthol was used for developing the colour. Zinc was determined by cutting out the appropriate portion of the chromatogram, ashing it and then assessing the zinc colorimetrically.

Barrows & Drosdoff (34) have described a fairly rapid polarographic method for determining zinc in 0.1N-hydrochloric acid extracts of mineral soils. An aliquot of the filtrate is treated with an ammonium chloride-potassium chloride-sodium sulphite-ammonia buffer (pH 11) prior to polarographic measurement.

Shaw (35) has described a wet-oxidation method using potassium dichromate-sulphuric acid-phosphoric acid for determining total carbon in soils, plant materials and aqueous plant extracts. Carbonate, when present, is removed by treatment with sulphurous acid.

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### FERTILISERS (D. P. Hopkins, B.Sc., F.R.I.C.)

#### Manufacture

IN the period of this report—1959 and 1960—probably the most interesting manufacturing development in Britain has been the expanded use of ammonium nitrate in compound fertilisers. The ammonium nitrate is produced at Messrs. Fisons' new factory in Essex as a hot concentrated solution (88%), and it is used as a part-source of nitrogen in compounding at a number of other factories sited in other parts of England, e.g., Devon, Yorkshire, etc., being transported from Essex in coil-heated road or rail tankers able to maintain a minimum temperature of 85° to prevent crystallisation. The costs of maintaining the fluid state are regarded as fully recovered by the advantages of fluid handling. A second feature of this new venture of 1959 is that the nitric acid conversion plant is virtually self-supporting for energy requirements, the heat released in the  $\text{NH}_3 \rightarrow \text{HNO}_3$  reaction being recovered for all needs except a few minor demands such as for pump operating. An initial



estimate of annual output of the Essex plant was 140,000 tons of ammonium nitrate per annum. The ammonia used is supplied by pipeline from a new and adjacent factory, the Shell Chemical Company's nitrogen works, which operates a fixation process based upon oil for fuel. Part of the ammonia produced is used for making 'Nitra-Shell' at this works. Total output has been said to be 75,000 tons of ammonia per annum. This addition to the country's nitrogen capacity began in 1959, when it represented an addition of about 15½% of current nitrogen fertiliser use. At the usual annual rates for expansion of nitrogen use, this might have required at least 3 years to absorb, but 1959-60 brought an exceptionally large increase in nitrogen usage—over 21%. The actual production increase—above that of 1958-59—was only some 13%. It would seem, therefore, that in one year this large additional home resource for fertiliser nitrogen has been fully absorbed. Indeed, in 1959-60 U.K. production of nitrogen was 19,500 tons less than home deliveries to farms. There have been numerous descriptive reports of the two new 1959 works (e.g., 1, 2).

Another new manufacturing development of the period has been the introduction by Imperial Chemical Industries Ltd. of a granular nitrogen-potash compound, 'KayNitro', which is particularly suitable for grassland or for ley-arable rotation land which has previously been well dressed with phosphate. Granulation without the plasticising help of a phosphatic ingredient has been regarded as difficult. The process being used has not been described, but a U.S. paper has reported a simple flowline for making and granulating N-K compounds (3); in this, the basic step is the pre-neutralisation of ammonia with acid and this precedes mixing with potash and granule formation.

The most prolific source of papers on granulation technology still seems to be the United States, where use of the process, having started later than here, is still energetically expanding. It must be borne in mind, however, that U.S. compound granulation problems differ because of the greater use of liquid nitrogen components—ammonia, nitrogen solutions, etc. In a comparison of two systems of granule drying—co-current and countercurrent—it was concluded that the latter consistently reduced the problem of fume formation (4). The greatest amount of decomposition, the cause of fume formation, occurs at the dryer throat where the hot gases enter. With co-current drying there is greater decomposition because the moist material at this point can adhere to the feed chute and feed lifters. With countercurrent drying such decomposition as occurs is only due to dust particles being carried by eddies into or close to the furnace. It was also found that countercurrent drying required a smaller fuel input.

Another paper has revived interest in the pan method of granule formation (5), where an inclined pan is used for continuous pro-

cessing. The pan rotates at 14 r.p.m. and is set at 30–50° from the horizontal. Larger particles migrate to the bed surface on the edge of the lower rim, from where they are discharged; smaller particles remain on the pan until they have gained sufficient size to migrate to this point of removal. It is claimed that a product of high uniformity of size can be obtained, but there is a larger risk of loss of ammonia than in the rotary shell method. This 'Flying Saucer' method of granulation is being used in Canada for low-N, high-P and high-K compounds, and it is also said to be considerably used in West Germany.

The technology of granulation has developed without much aid from, or appeal to, pure science, and a British contribution of 1959 (6) has dealt with the fundamental principles and problems of granule formation with simple mixtures of sand, salt and moisture. This paper has posed the questions: (a) why should a moist powder when vibrated on a plane surface or rotated in a drum form spherical granules, (b) why should such granules have appreciable mechanical strength and a density comparable to that produced by heavy applied pressures? The large gap between pure scientific knowledge about granulation and the empirical development of granulation in the fertiliser industry as a conditioning process almost certainly holds answers to a variety of operative anomalies, and if this gap can be narrowed better methods of processing may well emerge. Another Fertiliser Society paper (7) has described the new Dutch State Mines process for granulated calcium nitrate; droplets of concentrated solution are seed-crystallised during a short fall through mineral oil, the oil being later removed by centrifuging. A thin residual film of oil remaining on the granules is highly effective in giving good non-caking properties.

Sixty years ago it was suggested that phosphonitrilic compounds might have effective fertilising properties. TVA research (8) has produced NP products by burning elementary phosphorus in air and ammoniating the resultant phosphoric acid at 250–350°. A whitish fluffy powder is obtained, with N about 17% and  $P_2O_5$  80%, probably a mixture of ammonium metaphosphate, phosphonitrilic acid and the ammonium salt of the latter. Preliminary tests have shown good physical properties and excellent crop responses. Late in 1960 some details of a new British process for manufacturing granular potassium metaphosphate were given (9). This is another chemical substance whose use as a fertiliser has been only of academic interest for some decades. The process is a circulating bed reaction at about 450° between phosphoric acid and potassium chloride. It is claimed that the major economic disadvantages of earlier potassium metaphosphate processes have been overcome, e.g., high temperature requirement, severe corrosion difficulties and the fused condition of the product.

Finally a plea has been made for abandoning the fairly new descriptive term 'complex fertilisers' for certain classes of compounds (10). The word 'complex' is itself misleading, and it is doubtful whether it is justifiable to distinguish between mixed NPK products and those in which two of the plant foods have been chemically combined during manufacture, e.g., the nitrophosphatic compounds. In any case, the 'complex' NPK products still rely upon ordinary additive mixing for their potassium content. This plea has now been strongly supported by an eminent TVA fertiliser scientist (11). However, it must be noted that during 1959-60 FAO documents have been using and therefore recognising the new term. The fertiliser terminology inherited from the pre-1940 period is far from satisfactory, yet the modern European industry seems ready to add yet another misnomer.

### Use of fertilisers

One of the most significant studies of 1959-60 has been the O.E.E.C. study of optimum fertiliser use (12). For each country actual use of fertilisers has been compared with the tonnage that would be required if optimum rates were given to all crops and grass. The optimum rate, crop by crop, is defined as 'that dressing which gives the largest net profit if present economic conditions are maintained'. The data and calculations were based, however, upon 1956-57. This new comparison of national fertiliser consumptions emerged:

<i>% of optimum represented by actual use, 1956-57</i>			N	P	K
Belgium	..	..	68	75	91
Denmark	..	..	64	82	79
W. Germany	..	..	73	78	81
Netherlands	..	..	71	over 100	over 100
Sweden..	..	..	71	58	61
Ireland..	..	..	20	21	19
France ..	..	..	31	33	24
United Kingdom	..	..	51	80	56

Thus, by better European standards, only our use of phosphate had a good rating. These comparative figures obscure the further point that in some countries the optimum rates for grassland were higher than those for British grass—simply because utilisation of grass was of a higher standard, e.g., the Belgian optimum rate for N on temporary grass for hay was nearly three times the British optimum rate.

These assessments of use, like average rates per acre for national use, do not distinguish between crops that actually receive fertilisers and crops that are grown without any fertilisers. Often it is

non-use that pulls down national figures. A market survey (13) by one of the principal British manufacturers, carried out over about 4 years up to 1959, showed that these percentages of U.K. acreages received a *compound* fertiliser:

<i>Crop</i>				%
Cereals	..	..	..	71
Potatoes	..	..	..	94
Sugar beet	..	..	..	94
Brassicæ	..	..	..	73
Temporary grass	..	..	..	30
Permanent grass	..	..	..	11

The restriction of this survey to compound use is not seriously limiting for a country where mixed fertilisers are so predominantly applied to arable crops; for grassland, however, even when the use of straight fertilisers is included, the percentages of use are raised only to 60% for temporary grass and to about 40% for permanent grass.

These assessments are of *past* usage, however. One of the major difficulties in discussing national use of fertilisers is that it takes considerable time for reliable data to be collected and collated. For the farming year of 1959-60 there has been a sharp advance in U.K. use, one of unexpected size, and at present its interpretation can only be conjectured. Figures for total use in 1958-59 and 1959-60 (provisional) are as follows:

			1958-59	1959-60	Increase, %
			(thousands of tons)		
N	..	..	340.3	414.6	21.7
P <sub>2</sub> O <sub>5</sub>	..	..	384.9	458.8	19.2
K <sub>2</sub> O	..	..	375.2	426.2	13.6

Does this mean that at long last pleas for increased fertiliser use on grass have achieved more than slight success? A good deal of the advance for phosphate can be explained by an increase of more than 25% in supplies of basic slag; this is, of course, mainly a grassland fertiliser. Much of the total NPK increase must, however, be attributed to compound fertilisers; from 1958-59 to 1959-60 compound consumption *tonnages* rose by 13%. As NPK contents of compound fertilisers are steadily rising each year this is, in effect, at least a 15% rise in use of compound types. As, therefore, we must interpret much of the 1959-60 rise in terms of 'compounds', can this be attributed largely to expanded fertiliser use on grassland? The market survey data cited above suggest that of the temporary grass given fertilisers, about half receives 'compounds' and half receives 'straights'; but for permanent grass, a third receives 'compounds' and two-thirds receives 'straights'.

On the other hand, another survey in 1957 (14), recently published, has shown that 37% of 652 grassland farmers interviewed used 'compounds' on grass. If since 1957 the trend to use 'compounds' on grassland has become bolder, then we can perhaps guess that about half of the increase in NPK consumption for 1959-60 was applied to grassland. Unfortunately the second half of the 1959-60 season proved the wettest for many years, and as this weather effect mainly occurred after fertiliser applications had been given, the benefits of the extra use, whether on grass or cereals, have not been obvious. In terms of weather 1959-60 could not have been a worse year for demonstrating the merits of higher fertiliser use, and this could slow the further tempo of advancement.

Another useful study of British fertiliser use has come from the industry (15), largely a collation of statistics about post-war use, with special emphasis upon the 1950's. This showed that in the second half of the 1950's nitrogen use rose by 31.2%, phosphate by 9.5% and potash by 41.8%—but this calculation excludes the sharp rise for 1959-60 already mentioned. 'Compound' use rose in tonnage by 19.1%, but in terms of NPK content the compound share of total NPK applied rose from 64.7 to 70.1%. The production of compounds with higher total NPK contents has clearly been welcomed by farmers. In the period 1952-55 the average total NPK content of 'compounds' used was 27.66%; by 1958-59 this had become 32.48%. This study provided data of usage for seven English regions and for Wales, Scotland and N. Ireland.

An American survey of garden (or non-farm) usage in six New England states merits brief mention (16). The most revealing result was that lawn use accounted for 57% of total garden use; vegetables accounted for 26.7% and flowers 11.4%. The predominance of lawn use can be partly explained by the larger area taken up by grass in many gardens, but it must also be deduced that the 'appearance' factor motivates fertiliser purchases for lawns even where little fertiliser is used on vegetable or flower plots. The survey showed that about seven-eighths of the garden fertilisers used were chemical in kind, with compound types dominating. Reasons for non-use were probed and it was clear that in many cases sheer ignorance or timidity in choosing a suitable fertiliser was the principal cause. A lack of informed advice at points of sale was frequently mentioned. The broad findings of this unusual survey may well be true for most residential areas in developed countries.

The limitations of soil sampling and testing as a guide to fertiliser use have been very thoroughly discussed (17) and new data for variations in results due to positions of core-sampling and to times of sampling were presented. It was shown that the risk of error arising from sampling is ten times greater than the risk of error from laboratory analysis. The skill and experience of the

adviser who interprets test results is the most important element in the relationship between soil testing and fertiliser recommendation. Almost an ethical problem is posed by this subject. Clearly, advisers and soil scientists should know and discuss the limitations of soil testing with the utmost realism; yet if farmers are equally aware of the uncertainties their faith in what is still the best method for estimating fertiliser needs may be too severely damaged. However, farmers who regularly use fertilisers perhaps rely less upon soil test guidance than is supposed; in a survey already referred to (14), 49% selected fertilisers on the basis of past experience of their own experiments, as compared with 24% who chose fertilisers from soil test results. This indication came from a sample of grassland farmers using 'straights'; its wider applicability could be doubtful because of the absence of any reliable and simple test for nitrogen needs.

The use of liquid nitrogen fertilisers, and to a smaller extent of liquid NPK compounds, is steadily developing in the U.S.A., but in the U.K. the trend not to use solid fertilisers is minute by comparison. In a re-investigation of liquid nitrogen fertilisers on arable crops and grassland (18) under British conditions it was concluded that arable yields were closely the same with solid or liquid sources of nitrogen, and that for grassland the liquid fertilisers generally gave lower dry matter yields. As there were application problems with the liquid products—liquid ammonia, ammonia liquor, and two solutions based on ammonium nitrate and urea, ammonia and urea—advantages from using liquid fertilisers could not be established.

Forestry fertiliser problems have been much clarified since the mid-1940's, when the Forestry Commission concluded that even young trees differed from arable crops in their nutritional needs. A new paper (19) has summarised forestry research from 1945 to the late 1950's, and it is now clear that young trees from their seedling stage show growth benefits well related to NPK supplies, whether given in composts or as fertilisers. The 'Nitro-Chalk' type of fertiliser is now established for top-dressing young conifers, and phosphatic fertilisers have been shown to give consistently high responses on the acid soils commonly used for growing nursery stock. Responses to potash have been found at several centres. Forestry practice today is very similar to that followed for cereals, notably for winter wheat. The earlier and temporarily supported view that organic nutrition was essential and that chemical sources of nutrients could be harmful was based upon faulty experimentation and has now been completely dismissed.

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## HORTICULTURE (C. Bould, M.Sc., Ph.D.)

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### Nutrition

#### *Foliar diagnosis*

It is known that a number of factors such as season, age and position of plant organ, size of crop, etc., all affect plant composition. Specht (1) now suggests that variation in element concentration may aid in clarifying interpretation of plant composition. He postulates that plants possess a mechanism which controls degree of variability of element concentration in tissues. This hypothesis embodies the following concepts: (a) the degree of variability in concentration of a given element is related to the level of con-

centration of that element in plant tissues; (b) the action of the variation-control mechanism produces element-variability patterns that define optimum growth ranges for nutrient elements; and (c) the magnitude of element interaction phenomena is subject to the action of the variation-control mechanism. Concepts (a) and (b) were demonstrated experimentally for Mg in rose clover, for P in soya-bean and for Mn in rice. Relating variability and growth patterns, it was shown that the low concentration-least variation point occurs near the central portion of the poverty adjustment growth range; the region of higher variation corresponds to the luxury consumption range of the growth curve, and the high concentration-least variation point falls within the toxic effect range of the growth pattern. For example, the optimum growth-response range for rose clover lies between the two least-variation points of the variability pattern. From this it would seem that a low coefficient of variation for a given element, in replicate plant samples for the same plot, would indicate that the element was in low or high supply.

Mason & Whitfield (2) studied the seasonal changes and distribution of mineral elements in 5-years-old Malling IX apple trees on Malling IX and Malling XVI rootstocks, at monthly intervals. They found two periods of special activity, at the end of April and at the end of June, when the concentrations of the five elements, N, P, K, Ca and Mg, changed appreciably. These two periods coincided with the onset of rapid leaf growth, and of shoot growth. The uptake of most elements commenced at the end of April or May, and reached a maximum at the end of July or August, after which there was a loss of nutrients by the tree. There was no net absorption of nutrients during the autumn. At the end of the summer the bulk of each element in the tree was contained in the following organs: N in the leaves, branches and roots; P in the leaves, branches and roots; K in the leaves and branches; Ca in the leaves and bark; Mg in the leaves.

Bould *et al.* (3) studied methods of sampling and sampling errors in apple, blackcurrant and strawberry based on ten replicate samples (varying from 40 to 50 leaves) of each crop from uniform sites. They recommend that leaf samples should be taken without the petiole attached if sub-samples are to be used for analysis: this is due to the variation in composition between petiole and lamina and the difficulty of obtaining a representative sub-sample in the presence of petioles. Statistical treatment of the analytical data from the samples indicated that one field batch sample (of 40–50 leaves), one sub-sample and single analyses carried out on two analytical samples was a satisfactory compromise between speed and accuracy. With this sampling technique the overall sampling error, expressed as the coefficient of variation, was of the order of 6%, of which about 1.2% occurs at the analytical stage. No



significant reduction in sampling error was obtained by grinding the whole of the batch sample and taking samples direct for chemical analysis. In pot culture studies leaf-disc samples were used and found to be satisfactory.

In leaf analysis work, particularly when dealing with trace elements, it is important that the leaves should be free from surface contamination due to dust and sprays. Any washing treatment should remove both these sources of contamination and at the same time cause no loss of internal nutrients by leaching. Arkley *et al.* (4) compared two leaf washing techniques: (a) 0.1 N-hydrochloric acid for 30 sec. followed by three quick washings in distilled water, and (b) 0.1 N-hydrochloric acid plus detergent for 30 sec. followed by four rinses in distilled water. Control plants were grown in a dust-free greenhouse. Contaminated plants were dusted with a peaty loam and sprayed with a synthetic solution of trace elements. Contamination from sprays was less easily removed than that due to dusts; Fe, Cu and Zn spray residues were removed effectively by the washing procedures, but Mo and Mn were more difficult to remove. There was no loss of internal nutrients by leaching, and both treatments were equally effective.

Bould (5) studied the effect of NPK fertilisers, at two centres, on the growth, crop yield and chemical composition of leaves of blackcurrant. At one centre he found that increasing amounts of ammonium sulphate, over the range 3.9 cwt./acre, depressed growth and yield of fruit. This was shown to be due to soil acidification, which in turn depressed the availability and uptake of soil-P. In leaf samples, taken from the mid-third region of extension shoots at the fruit-ripening stage, the leaf-P concentration, for the variety Baldwin on the 'no-phosphate' plots, was 0.21% in dry matter. The corresponding value for the variety Mendip Cross was 0.20%. These values were too low for optimum growth and crop yield. At the second centre, where bushes failed to respond to phosphatic fertiliser, the leaf-P concentration in both varieties was  $\geq 0.3\%$  in dry matter. The optimum concentration would appear therefore to lie between 0.24 and 0.3% P in dry matter. In the same experiments it was shown that a leaf-K concentration of 1.5% in dry matter was adequate for normal growth, whereas values  $< 1.0\%$  K in dry matter were inadequate.

Eaves *et al.* (6) investigated the effect of dolomitic limestone on the cation relationships in leaves, bark and roots of Cortland apple trees. They found that the addition of limestone resulted in a general increase in the levels of Mg, and a decrease in the levels of K and Ca. The established negative relationship between K and Mg in the leaves was not found in either the bark or roots, thus supporting Lundegårdh's statement 'that the degree of ion antagonism in one organ of the plant is independent of the behaviour in another organ'.

*General nutrition, deficiencies and excesses*

Concern is felt in many parts of the world over the fall-out from atomic explosions and the effect of the radioactive isotopes taken up by plants and ultimately consumed by animals. Plants accumulate radioactive strontium, a product of nuclear fission, from soils contaminated with fall-out from atomic explosions, or waste products from nuclear reactors. In considering means of reducing crop uptake of  $^{90}\text{Sr}$ , the application of calcareous fertiliser to contaminated soil appears to be the most hopeful and practical treatment. Romney *et al.* (7) showed that additions of calcium carbonate and sulphate to an acidic soil reduced  $^{90}\text{Sr}$  uptake, and that rates of 2-5 tons per acre of calcium carbonate were most effective. Neither form of calcium reduced uptake of  $^{90}\text{Sr}$  from a neutral soil, or from a calcareous alkaline sandy loam. It appears that further additions of Ca will provide little protection against uptake of  $^{90}\text{Sr}$  from Ca-rich soils. In other experiments it was shown that additions of stable Sr, as nitrate or sulphate, increased the uptake of  $^{90}\text{Sr}$ . Stable Sr displaced  $^{90}\text{Sr}$ , adsorbed on the exchange complex, into the soil solution where it was more readily available to the plant. This effect was most marked on acidic soils.

Because of its long half-life and its close relation to K in certain physico-chemical reactions,  $^{137}\text{Cs}$  is considered to be one of the biologically significant fission products. Nishita *et al.* (8) studied the effect of K and stable Cs on the uptake of  $^{137}\text{Cs}$  by Ladino clover from contaminated soils. The addition of K to soils containing relatively high levels of K was ineffective in reducing  $^{137}\text{Cs}$  uptake by plants, but after the soil-K had been reduced to a low level by cropping, the addition of K to soils reduced uptake of  $^{137}\text{Cs}$  by plants. The addition of small amounts of stable Cs to soil markedly increased uptake of  $^{137}\text{Cs}$  and reduced uptake of K by plants. It would appear therefore that K was antagonistic to the uptake of Cs.

The frequent appearance of Mg-deficiency symptoms in mature leaves has been the basis for a hypothesis that Mg is mobile within the plant, and is readily redistributed from old to young leaves. Recent work, however, suggests that the appearance of symptoms in mature leaves does not constitute evidence for mobility and redistribution. The immobility of the radioactive alkaline earth cations calcium, strontium and barium, has been demonstrated, and the recent availability of  $^{28}\text{Mg}$ , with a half-life of 21.3 hours, has made it possible to study the mobility of Mg. Bukovac *et al.* (9) have studied the absorption and distribution of  $^{28}\text{Mg}$  in bean seedlings.  $^{28}\text{MgSO}_4$  solution, adjusted to pH 2.0, was applied to the upper surface of the primary leaf blades and plants were harvested after  $\frac{1}{2}$  h. up to 24 h. and assayed for  $^{28}\text{Mg}$ . Approximately 10% was absorbed and recovered in the primary leaf after

24 hours. No significant amount of radioactivity was detected in the remainder of the plant, indicating that  $^{28}\text{Mg}$  was not translocated out of the treated leaf. This was confirmed, using more mature fruiting plants. The authors suggest that the high requirement of the meristem and developing seeds for Mg may result in preferential transport of root-absorbed Mg to these tissues. Under conditions of mild, or severe, deficiency this may reduce to a critical level the flow of Mg to the mature leaves. Furthermore, some cell-Mg may be rendered inactive by reaction with cell-wall constituents (e.g., magnesium pectate). With limited supplies of Mg, chlorotic areas would develop most readily in the interveinal areas of mature leaves and produce the typical symptoms of Mg-deficiency.

Bitter pit in apples has been a serious problem in certain varieties for many years. The influence of moisture stress, fruit size, crop size and nitrogen level in determining the incidence of bitter pit in apples is now generally accepted, but evidence for the effect of mineral nutrients is still very conflicting. From time to time it has been suggested that boron and phosphorus were associated with this disorder. More recently, Garman & Mathis (10) have carried out experiments on Baldwin Spot, a disorder probably identical with bitter pit, which indicated that Ca-level was an important factor in determining incidence, and that antagonistic effects could develop between Ca and Mg. They obtained responses from late summer sprays and from soil injections of calcium salts. They proposed the hypothesis that in times of water stress the leaves might compete successfully with the fruit for Ca. Martin *et al.* (11) tried six different spray treatments (0.1% solutions) in relation to the incidence of bitter pit in apple. The main results were as follows: magnesium nitrate increased and calcium nitrate decreased pit, calcium dihydrogen phosphate had no significant effect with or without borax. Their results support those of Garman & Mathis, namely, that the critical element is calcium and the unbalanced condition lies between calcium and magnesium. No explanation can be offered as to why Ca as the nitrate should reduce pit and Ca as the dihydrogen phosphate should not, especially in view of the fact that nitrogen application usually increases pit and phosphate has been reported to reduce it. It was shown that calcium nitrate sprays more than doubled the Ca concentration of the fruits. Further evidence relating Ca to bitter pit has been reported by Askew *et al.* (12). They carried out detailed chemical investigations on bitter pit of apple in relation to foliar sprays of the acetates of Ca, Mg, K and Na, and of superphosphate and borax. Analyses showed that the sprays altered the chemical composition of fruit and leaves. In one season, a calcium acetate spray significantly reduced the amount of bitter pit in Cox's Orange Pippin apples but was not significantly beneficial in a second season.

Potassium in three trials was very detrimental and significantly increased the incidence of pit; Na and Mg were also detrimental. High dry matter, high ash contents and high K/Ca ratios in the fruit were associated with increased incidence of bitter pit. High Ca values and high Ca/K ratios were associated with a reduction in bitter pit.

Cobalt as an essential element for animals and various micro-organisms centres around the rôle of vitamin B<sub>12</sub>. This vitamin is required by most animals in the formation of haemoglobin and may also be concerned with protein synthesis. Many micro-organisms require preformed vitamin B<sub>12</sub>, others, including *Rhizobia*, produce the vitamin. Cobalt has not been demonstrated as essential for the growth of higher plants, although it has been shown to be essential for blue-green algae. With higher plants, Co-supplements have been reported to increase growth of rubber plants and tomatoes, and more recently it has been suggested that soya-bean plants grown with symbiotically fixed nitrogen as their only source of this element distinctly benefited from small quantities of Co. Reisenauer (13) has now shown that Co plays an essential rôle in symbiotic nitrogen fixation in lucerne (*Medicago sativa*). Addition of Co to purified solutions increased plant growth by 66% and considerably increased nitrogen fixation. Ahmed & Evans (14) have also studied the effect of Co on the growth of soya-bean plants under symbiotic conditions with *Rhizobium japonicum* in the absence of combined nitrogen. Plants in culture solution without added Co were severely retarded in growth and displayed a leaf chlorosis similar to that caused by N-deficiency. The addition of 0.1–1.0 part per billion of Co resulted in normal vigorous plant growth. No evidence was obtained that V, Ni, Ga or Al would substitute for Co. It was concluded that Co is an essential element for the growth of soya-bean plants under symbiotic conditions in the absence of combined nitrogen.

The occurrence of Mo-deficiency in fruit crops under field conditions is rare. Stewart & Leonard, in 1951, reported that the 'yellow spot' disease of citrus in Florida is caused by a Mo-deficiency which can be remedied by foliar sprays of sodium or ammonium molybdate. Hoagland, some years ago, induced Mo-deficiency in plum grown in nutrient culture, and now Fernandez & Childers (15) have induced Mo-deficiency in seedling apple. The plants were grown in nutrient culture without Mo for 8 months, during which time the growth remained normal. After hard pruning, the new growth showed deficiency symptoms, first a mild uniform chlorosis, then, with increasing age, a tip burn which spread rapidly along the leaf margin accompanied by a downward cupping of the leaves. Leaf analysis showed that deficient plants contained 0.05 p.p.m. of Mo in leaf dry matter compared with 0.16 p.p.m. Mo in normal plants.

Gerloff *et al.* (16) studied the Mo-Mn-Fe antagonism in tomato plants grown in water culture. Mo was found to accentuate Fe-deficiency. The authors suggested that this is due to the formation (in the roots) of Fe-Mo precipitates of very low solubility, which prevents translocation of Fe to the tops. High concentrations of Fe render Mo unavailable. These two facts may help to explain Mo-deficiency in acid soils and Fe-deficiency in alkaline soils.

Liebig *et al.* (17) investigated the effects of potassium arsenate and arsenite on citrus grown in nutrient solutions. They found that 1 p.p.m. of As as arsenate or arsenite stimulated root growth; 5 p.p.m. of As as arsenite and 10 p.p.m. of As as arsenate were definitely toxic and adversely affected both root and top growth. The only unusual leaf symptoms were necrotic spots which developed during hot weather. Vein chlorosis, generally indicative of root injury, also developed under toxic levels. The maximum concentrations of As found were 11 p.p.m. in old leaves and 1200 p.p.m. in root dry matter.

### Foliar sprays

Generally speaking, the sulphates of nutrient elements are used as foliar sprays. It was shown by Fisher & Walker, in 1955, that Mg can enter apple leaves most readily from nitrate and chloride solutions, least readily from sulphate and phosphate, and at an intermediate rate from acetate. In 1956, Oland & Opland found that Mg entered the leaf more readily from acetate than from sulphate, but the acetate caused damage to the leaves. Recently, Allen (18) carried out experiments with apple leaves to study the effect of sulphate, chloride and nitrate on the uptake of Mg. When leaves were dipped in 0.1M solutions and allowed to dry, Mg was taken up more readily from nitrate and chloride than from sulphate. However, when leaves were left immersed in 0.1M solutions for varying periods of time the uptake of Mg was equally rapid from all three salts. At 20° the relative humidity of air in equilibrium with saturated solutions of magnesium sulphate, acetate, nitrate and chloride is 82, 65, 55 and 33% respectively: under the experimental conditions it varied from 72 to 52%. Magnesium chloride would therefore have remained in solution throughout the duration of the experiment, nitrate throughout part of the time whilst sulphate would have crystallised out. Allen suggests that differences in uptake from the salts can be explained in terms of relative humidities at the time of the experiment.

Foliar sprays of 1% magnesium nitrate were more effective than sulphate or chelate in controlling Mg-deficiency in orange trees (19), but Mg-deficient celery would not respond to soil dressings of 400 lb./acre of magnesium sulphate, although it was controlled by 1% foliar sprays (20). Chlorosis in celery occurred when the leaf-Mg was <0.1% in dry matter.

It is usual for 0.5–1% urea foliar sprays to be applied to young leaves for the correction of nitrogen deficiency; young leaves having been shown to be more effective absorbers per unit area than old leaves. It is known also that prior to leaf abscission some nitrogen is translocated back into trees. Oland (21) has now found that a 4% solution of urea sprayed on apple trees in the middle of October, about a month before leaf-fall, increased the N-content of leaves by 51% within 2 days of application. By leaf-fall a considerable part of the absorbed urea had been translocated to other parts of the tree. Spur-N had increased by 31% and terminal shoot-N by 16%. Leaf injury due to the spray was slight.

In 1958 Kessler & Moscicki reported that tri-iodobenzoic acid (TIBA) promoted the mobility of iron and calcium applied in foliar sprays to tomato plants and apple trees. Bar-Akiva & Hewitt (22) have not been able to confirm this effect on deficient citrus seedlings, and found no beneficial effects from TIBA on the absorption of foliar sprays of ferric chloride or ferrous sulphate. The inclusion of 2% urea in the sprays resulted in a more uniform production of chlorophyll in leaves sprayed with iron. Urea, however, did not promote any movement of iron within the leaf or from one leaf to another. It was concluded that urea promotes more uniform penetration of foliar-applied iron salts.

#### Iron chlorosis and iron chelates

It is known that iron chlorosis may be induced by a number of factors, including a shortage of iron, excess calcium, excess heavy metals and high bicarbonate concentration. It was shown by Harley & Linder, in 1945, that the bicarbonate content of irrigation water was related to the incidence of chlorosis in certain apple and pear orchards. It is known also that the respiration rate of susceptible crops is lowered by the presence of bicarbonate ions, which reduce the activity of cytochrome oxidase. It is not known, however, whether the bicarbonate *per se* is responsible for iron chlorosis or whether the effect is indirect. Using a divided root technique, in which the iron source (soil) was separated from the bicarbonate source (nutrient solution), Brown *et al.* (23) have shown that bicarbonate maintains higher concentrations of phosphorus in solution. This enhances the uptake of phosphate, which in turn causes chlorosis. In studies using iron ethylenediaminebis-(*o*-hydroxyphenylacetic acid) as the source of iron, Hale & Wallace (24) found that bicarbonate and phosphate both competitively inhibited iron accumulation. This suggests that both these ions compete with the Fe chelate anion for absorption on specific absorption sites.

Kessler (25) investigated the relationship between the respiration rate of fruit tree roots and their susceptibility to lime-induced chlorosis. He found an inverse relationship between CO<sub>2</sub> output of

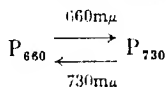
roots and their lime tolerance. The results were interpreted on the basis of the hypothesis that chlorosis-inducing bicarbonate ions are produced by interaction between carbonate in the soil and respiratory  $\text{CO}_2$  at the soil-root interphase, thus relating lime-induced chlorosis to the respiratory activity of the roots. He suggests that respiration rates of roots might be used as criteria for the selection of lime-tolerant stocks.

Brown & Tiffin (26) have attempted to relate the capacity of a plant to absorb Fe from Fe-chelate to its susceptibility to iron chlorosis. Chlorosis-susceptible (PI) and non-susceptible (HA) soya-beans were used as test plants and ethylenediaminebis-(*o*-hydroxy-phenylacetic acid) as the chelating agent. HA roots absorbed more Fe from the nutrient solution than did PI roots. Increasing the P-concentration of the nutrient solution decreased Fe uptake to a greater extent with PI than with HA roots. With the mixed radio-isotopes  $^{55}\text{Fe}$  and  $^{59}\text{Fe}$  in nutrient solutions and decapitated soya-bean plants, it was found that the exudate from the HA plants contained more radioactive iron than did the exudate from the PI plants. Furthermore, much of the chelating agent remained in the nutrient solution after absorption of Fe. The authors suggest that susceptibility to chlorosis in plants may be related to the metabolic processes involved in the separation of Fe from Fe-chelate, and that roots, phosphate and chelating agent may all be competing for Fe at the root surface.

By a divided root technique, Tiffin *et al.* (27) investigated the effect of absorbed chelating agents on the subsequent absorption and translocation of iron in soya-beans. There was a small effect on the absorption of radioactive Fe from soil, and on the translocation of foliar-applied radioactive Fe, but the effects were not sufficient to correct Fe-chlorosis. They suggest that the primary rôle of iron chelates in plant nutrition appears to be that of making iron soluble and available to the roots for absorption. Absorbed chelating agent is not an effective activator of iron from within the soya-bean plant.

### Flowering

Photoperiodism, as a control of flowering, was discovered by Garner & Allard in 1918, but the mechanism involved has only recently been explained by Borthwick & Hendricks (28). It is due to a pigment called 'phytochrome', a blue or bluish-green pigment that exists in two forms interconvertible by light thus



where 660 and 730  $\text{m}\mu$  are the absorption maxima of the two forms. Form  $\text{P}_{730}$ , which is enzymically active, changes in darkness to the

inactive form  $P_{660}$  in the course of some hours, and the rates of change and the enzymic action are essential factors in the plant's measurement of night light. The enzymic reaction controlled by  $P_{730}$  also affects many aspects of plant growth besides flowering, and results in a general control of growth by light. Phytochrome is present to the extent of 1 part in 10 million in many plant tissues.

Kessler *et al.* (29) have investigated the effects of various purines and pyrimidines on the flowering of several fruit species and annual plants. Uracil, xanthine and caffeine at 50 p.p.m. were active, while adenine and guanine had no effect on flowering. It is suggested that the effect of the flower-promoting purines and pyrimidines comes about through their enhancing effect upon the synthesis of the flowering hormone which apparently takes place in the leaf.

### Plant constituents

Beet processors have been troubled by the sporadic occurrence of a bitter off-flavour in processed beets. This flavour is absent in raw beet, suggesting that its formation is heat-induced. Recent studies have related this off-flavour to a high concentration of pyrrolidonecarboxylic acid (PCA). Glutamine, the precursor of PCA, is tasteless, and accounts for the lack of off-flavour in raw beet. Based on experiments with tomato, it was thought that the excessive use of ammonium fertiliser might be connected with a high glutamine content of the beet and hence have a bearing on the development of off-flavour. Shallenberger & Sayre (30) found no differences between sources of nitrogen. Increased rate of application of nitrogenous fertiliser may, however, significantly increase the PCA content of processed beets compared with plants receiving low rates of nitrogen.

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### ANIMAL NUTRITION (J. Davidson, B.Sc., Ph.D., A.R.I.C.)

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#### Energy

The genetical inheritance of an animal sets the upper limit to productivity, but production near this upper limit can be achieved only when the environment and nutrition of the animal are suitable. A suitable environment is brought about by good methods of management and suitable nutrition by providing a diet containing all the essential major and minor nutrients in the proportions most favourable for that particular production.

#### *Nutrition during the rearing of cattle for milk production*

The nutrition of the cow up to the age of first calving may have a profound effect on subsequent milk production, no matter how generous or well balanced the ration of the animal during lactation. It is of importance therefore to know which of the many systems of rearing dairy herd replacements will allow full achievement of

genetic potential. Some systems of rearing allow a steady and rapid rate of growth, while others, which have perhaps become more common in recent years with the introduction of early weaning, allow slower rates of growth, sometimes with marked fluctuations in body weight gain.

A recent long-term study (1) with twin cattle provides further information on the effect of plane of nutrition during rearing on the subsequent performance of the cow. Eighteen pairs of identical and six pairs of fraternal twin calves of Friesian and Ayrshire breeds were reared on the following systems:

- HH A continuous high plane of nutrition from birth to first calving with 110% of the standards suggested by Ragsdale (2) fed after weaning.
- LL A low plane from birth to 2 months before calving with 70% of the Ragsdale standards fed from weaning to 6 months and 60% to 2 months before calving.
- HL A high plane for the first 10 months of age followed by a low plane to 2 months before calving.
- LH A low plane for the first 10 months of age followed by a high plane to first calving.

The HH treatment provided allowances similar to those suggested by Roy (3) for maintenance plus 1 lb. live weight gain per day, and the LL treatment provided just over half these amounts. Typical rations are given in Table I. One main difference from 6 months of age was the absence of concentrates from the low-plane rations.

**Table I**

*Typical rations during rearing*

Age months	Concentrates, lb./day	Seeds hay, lb./day	Oat straw, lb./day	Swede turnips, lb./day	Grass silage, lb./day
<i>High plane</i>					
1	4	5½	—	10	—
10	2	9	—	—	23
18	4	—	12	—	36
24	5	10½	—	57	—
<i>Low plane</i>					
1	2½	2½	—	6	—
10	—	6½	—	—	11
18	—	—	9½	—	21
24	—	8½	—	39	—

From 24 months of age or about 2 months before calving, all animals were fed on the high plane of nutrition, which was equivalent to a 'steaming-up' regime. After calving, the allowances provided 6.5 lb. of starch equivalent (SE) with 0.7 lb. of digestible crude protein (DCP) for maintenance and 2.5 lb. SE with 0.5 lb. DCP for each gallon of milk produced. The allowances for maintenance were sufficient for an 1100-lb. cow according to 'Rations for

Livestock' (4) and appeared generous considering that the LL animals averaged 750 lb. and the HH animals 1000 lb. live weight at 24 months. However, it is essential to feed well just before calving, especially if the animals are not fully grown and therefore still making appreciable weight gains.

Results from this study showed that the animals on HH, LH, LL and HL treatments came into first oestrus in that order at 12, 14½, 16 and 18 months respectively. All animals were served at 18 months and calved around 27 months. This was 6 months earlier than the average time of first calving of Ayrshires and Friesians in the United Kingdom (5) and, if early calving following a low plane of nutrition during rearing interferes with subsequent development of the animal, stunting and perhaps reduced milking performance might have been expected on the LL treatment, but such detrimental effects were not noticed.

Subsequent to the HH, LL and LH treatments the production of fat-corrected milk (FCM) adjusted to lactations of average length was not significantly different during the first three lactations but production was significantly less during the first two lactations on the HL treatment. The total adjusted FCM yields for the three lactations were 18,700, 18,500, 18,900 and 16,500 lb. for the HH, LL, LH and HL systems of rearing respectively. Over the three lactations there were no significant differences in mean butterfat percentage or percentage of solids-not-fat.

The LL and LH planes of nutrition during rearing were therefore as effective in regard to milk production as the HH plane. Moreover it would appear from the most recent work (6) that animals fed at the low level throughout the rearing period give on average one more lactation before having to be discarded than animals fed at the high level. Elimination from the herd for various reasons would appear to be connected with body size or stage of development rather than age.

There can be no doubt that maturity is attained at a later date by cows reared on a low plane of nutrition, but provided this plane is not so low as to affect the vitality of the young animal, milk production will not be affected and the size ordained by genetic inheritance is eventually attained.

In the above study on planes of nutrition during rearing, there were no significant differences in the average live weights of the animals on each treatment after the 3rd calving at about 5 years of age and many other physical measurements of growth such as circumference of metacarpus and width of hooks were by that time not significantly different.

It is interesting to note that the cost of feed for rearing to first calving at 27 months on the HH, HL, LL and LH treatments were £59, £44, £31 and £51 respectively. However, when considering the saving on the low level of feeding it should be remembered that

calving on the HH treatment could have taken place some 6 months earlier than was actually the case.

A high plane of feeding followed by a low plane involving a sudden check in growth rate is not to be recommended because it may lead to late first oestrus and low milk yields, particularly in the first two lactations.

#### *Nutrition around parturition*

In another study (7) planes of nutrition were varied over a different period of the life cycle of the cow, namely from 1 month before to 3 months after calving. This work provides interesting information on the importance to production and efficiency, of providing extra nutrients around this time in the form of balanced concentrates.

Two levels of concentrates were fed in the rations just before calving and two levels for the first 84 days after calving. Before calving there were two groups of cows fed either on a high plane of nutrition, which included 2 cwt. per animal of concentrates spread over the 21 days before calving, or on a low plane of nutrition, which included  $\frac{1}{2}$  cwt. of concentrates spread over the 14 days before calving. After calving, half the animals on each pre-calving regime were fed on a high plane and the other half on a low plane of nutrition. The high and low planes after calving were at the rate of 5 lb. and 3 lb. concentrates respectively per gallon of milk produced in addition to the maintenance ration. From 12 weeks after calving all cows were fed at the normal rate of 4 lb. concentrates per gallon. The treatments could then be designated hh, hl, ll and lh, for which the milk yields were respectively 2770, 2720, 2730 and 2440 lb. over the first 12 weeks and 8220, 8170, 8090 and 6750 lb. over the whole lactation.

Thus the high level of concentrate feeding before calving ('steaming up') had a pronounced effect on subsequent lactation only when the production part of the ration after calving was below what is considered normal—4 lb. of concentrates per gallon of milk produced. Moreover, the effects noted during the experimental 12 weeks were carried over into the subsequent part of the lactation.

This study confirms that a 'steaming-up' regime prior to calving can have marked beneficial effects on subsequent milk production at low but not high levels of feeding after calving and may thus also indicate why evidence is sometimes conflicting (8) on the effects of 'steaming up' on subsequent milk production.

It would appear reasonable that round about the time of calving, when the alveolar cells in the udder are developing and beginning to secrete milk, production should not be hindered by a lack of nutrients. Once tissue has stopped developing the limit to milk production is set. Milk production depends on the number of

functional cells and these are maximal in early lactation when the milk yield is building up to a peak.

The demonstration of a 'steaming-up' effect may result from an inadequate plane of nutrition in the final stages of rearing or from an inadequate feed allowance for milk production immediately after calving. It might be argued that a beneficial effect from 'steaming-up' shows that the normal production allowance is inadequate at least for the early stages of lactation before peak milk yield is reached. As milk yield is rising rapidly during this time the feed production allowance should be based on expected yield by feeding, say, an extra 1 lb. or 2 lb. of concentrates per day in addition to the allowance calculated on the previous week's yield.

#### *Early weaning of calves*

From the above and other studies (9) on the plane of nutrition during rearing of dairy cattle it would appear that a low plane of nutrition during rearing is not necessarily detrimental to subsequent milk production, and this is reflected in the increasing interest being taken in early weaning whereby milk substitutes replace liquid milk for calves, thus freeing milk for human consumption. The calf, unlike the human, derives immunity to infectious diseases from the colostrum of the parent cow. Moreover the antibodies responsible for conferring immunity can pass into the blood only during the first 24-36 hours of life and so when attempts are made to rear artificially the calf should be left to suckle for a few days or should be fed colostrum from a bucket.

For the first few weeks after birth the calf functions like an animal with a simple stomach because when a liquid food is given the rumen is by-passed and the food is delivered directly to the abomasum or true stomach. At this time the calf is unable to digest appreciable quantities of starch because of the absence of the necessary enzymes (10). In fact even at 9 months of age, maize starch and ground maize given directly into the true stomach may be only partly digested, a large part being excreted in the faeces (11). It would appear that in calves dietary glucose and lactose are readily used during the first few weeks, whereas sucrose, maltose starch and dextrins are not (12). The former are thus more suitable carbohydrates for calves given milk substitutes or gruels that pass by the oesophageal groove to the abomasum and do not pass into the rumen.

### **Trace minerals**

#### *Selenium*

As previously mentioned in these Reports (13), Se was found to be an integral part of the 'Factor 3' from American dried brewer's yeast, which prevented liver necrosis in rats fed on diets deficient

in vitamin E. Ten  $\mu$ g. of Se as seleno-cystathionine or sodium selenite has also prevented exudative diathesis in chicks fed a *Torula* yeast diet free from vitamin E (14). The protective effect of L-cystine against dietary liver necrosis evidently stems, at least in part, from traces of a selenium compound in the amino-acid (15) and thus degeneration of the liver owing to necrosis is now attributed to the simultaneous lack of only two essential nutrients, namely, vitamin E and a selenium compound. However, methionine and cystine in excess of requirements may delay the onset of exudative diathesis as a result of some sparing action on the requirement for vitamin E (16).

Recent work with large animals shows that the addition of 0.1 p.p.m. of Se to practical ewe rations based on Ladino clover hay from an area where muscular dystrophy was widespread afforded protection against the disease in the corresponding lambs (17). The Ladino clover hay contained <0.1 p.p.m. of Se.

Other work (18) with lambs showed that diets of trefoil grass hay containing 0.06 p.p.m. of Se and raw cull kidney beans containing 0.01 p.p.m. of Se could be rendered less dystrophogenic by the addition of 1 p.p.m. of Se as sodium selenate, 100 i.u. of  $\alpha$ -tocopheryl acetate or linseed oil meal. The latter contained 1.2 p.p.m. of Se, its protective effect being associated with this trace element. The incidence of muscular dystrophy in lambs from ewes fed these diets from 1 month before parturition was 8 in 18, 1 in 21, 2 in 15 and 2 in 14 respectively for the control diet, and the diets fortified with selenium, vitamin E and linseed oil meal.

It has been shown in New Zealand (19) that oral administration of 5 mg. of Se to ewes 3 weeks before parturition gave partial protection to the lambs against muscular dystrophy whereas 300 mg. of  $\alpha$ -tocopheryl acetate administered orally gave none. Although some protection against muscular dystrophy was afforded by  $\alpha$ -tocopherol in a later study with lambs the effect was not so striking as with the addition of trace amounts of selenium, the losses attributable to dystrophy being 50 on the control diet, 21 on the diet with added vitamin E and 2 on the diet with added Se.

A preliminary report from New Zealand (20) shows that administration of 0.5–1 mg. of Se either by mouth or subcutaneous injection every 10 days may increase the growth rate of unthrifty lambs by 12–40% and thus be an important factor in the control of one form of unthriftiness occurring in New Zealand.

In other trials with lambs of around 40 lb. weight (21) from badly affected farms on which up to 10% of the lambs had been lost since 'marking', 5 mg. of Se as selenate was given by mouth at the start of the experiment, then repeated 2 weeks and 6 weeks later. At the end of the 10 experimental weeks mortality in the control groups was 27% compared with 8% in the groups dosed with selenium.

Treatment of unthrifty calves with Se in the same area resulted

in average weight gains of 27 and 21 lb. respectively for the control and treated groups over a 4-week period when the animals were about 8 months old (22).

Studies in the North of Scotland (23) have shown that Se administration at 0.25 mg. of Se/day may control the occurrence of muscular dystrophy in suckling beef calves as effectively as 200 mg. of vitamin E per week.

When considering the benefits to be derived from the addition of trace amounts of Se to the diet it is important to know the approximate toxicity level. This would appear to be 3-4 p.p.m. in the diet for the rat (16) and 5 p.p.m. in herbage for the ruminant (24), but it has been emphasised repeatedly that the toxicity of selenium depends greatly on the forms of Se compound present in the diet and on the nutritional status of the animal. A level of 10 p.p.m. in diets for the young pig has been found (25) to induce toxic symptoms, decrease conception rates, weaning percentage and weight gains of the offspring to 56 days of age. Diets containing this amount of selenium may occur in seleniferous areas where grain may have a Se content of 10-20 p.p.m.

### *Copper*

It is now well known that copper deficiency in cattle and sheep can occur despite an apparently adequate intake of copper in the diet. This may indicate the presence of factors in the food which interfere with the utilisation and storage of dietary copper.

It has been suggested (26) that added calcium and/or phosphorus may lead to reduced storage of Cu in the liver by the calf and also (27) that Mo and sulphate, the latter derived on occasion from a high-protein diet rich in sulphur amino-acids, may limit Cu retention in the sheep. Liver-Cu levels in sheep after 30 weeks on a basal diet containing Cu 5.2 p.p.m., Mo 0.8 p.p.m. and sulphate 0.04% were 240 p.p.m. on the dry liver. Raising the Mo to 5.1 p.p.m., the sulphate to 0.4%, or the Mo to 5.1 p.p.m. and sulphate to 0.4% in the diet lowered liver copper levels to 170, 70 and 25 p.p.m. respectively.

In Australia, supplements of molasses had a marked effect in preventing copper storage in the liver when the basal ration was a grass of low nutritive value (27). It is possible that this depression of liver-copper content by molasses may be explained on the basis of some factor or factors such as sulphate or molybdenum interfering with copper utilisation and storage.

The mechanism underlying the effect of Mo and sulphate in restricting Cu utilisation is as yet not completely clear. It may be that diets high in Mo and sulphate restrict Cu uptake from the digestive tract. Such diets also result (28) in diminished transfer of Cu to the foetus or possibly in a decreased transfer to the lamb during suckling.

When a high content of sulphate was present in the diet of the ewe, liver copper stores fell from normal values of over 200  $\mu\text{g./g.}$  of dry matter to 7–12  $\mu\text{g./g.}$ , and to 8–10  $\mu\text{g./g.}$  in the livers of the corresponding lambs (29). Addition of Mo as well as sulphate to the ewe diet resulted in liver Cu values of 23–32  $\mu\text{g./g.}$  of dry matter in the ewe and values as low as 3  $\mu\text{g./g.}$  in the lambs. Moreover, histological examination revealed damage to nervous tissue in the latter lambs similar to that found in field cases of 'swayback' or enzootic ataxia.

That Mo and sulphate are not the only factors involved in field cases is evident from studies at Weybridge (30), which have shown that on diets of hay and crushed oats which have a relatively high sulphate content, the liver-copper content of pregnant ewes can be raised by adding molybdenum.

Attempts to control copper deficiency in the field by top dressing of pastures with copper salts have met with mixed success and dosing calves and sheep by subcutaneous injection of 120 mg. or 45 mg. of copper respectively as the glycinate has been developed (31). In such procedures side reactions at the site of injection have sometimes been noted and because of this the cupric-bis-8-hydroxyquinoline-5,7-disulphonic acid salt of tetraethylamine (32), which does not give rise to these side reactions, may prove more useful.

In all these studies on copper, emphasis is laid on the importance of ensuring that a state of copper deficiency really exists in the animal before treatment with copper salts. Copper poisoning is apparently on the increase from indiscriminate use of mineral supplements containing copper, and from feeding to ruminants in error pig feeds supplemented with copper.

The feeding of high levels of copper of the order of 250 p.p.m. in the diet to pigs is now practised widely, following collaborative work reported from the National Institute for Research in Dairying in 1955 (33). Such inclusions improved feed conversion ratios and mean growth rates of bacon pigs. The toxicity level for the pig is between 250 and 500 p.p.m. under British conditions (34), a marked increase in liver Cu stores being noted when the diet contains more than 125 p.p.m. Cu.

The mode of action of dietary copper sulphate appears to be somewhat similar to that of antibiotics in that multiplication of certain micro-organisms in the intestine is affected, with subsequent benefit to the host animal. In the pig a decrease in coliform and lactobacillus populations (35) in the upper part of the duodenum seems to be involved.

Results contrasting with those obtained by European workers have recently been reported (36) from Australia, where 250 p.p.m. Cu in the diet caused a skin condition, parakeratosis, which is normally associated with Zn deficiency, and sudden deaths with post-mortem symptoms suggesting copper poisoning. American



workers have demonstrated (37) that high dietary Cu can reduce storage of Zn in the body, while others (38) have claimed that diets containing Cu may protect against parakeratosis!

### *Molybdenum*

It has been known for some time (39) that the ash of lucerne stimulates weight gains in ruminants when poor quality roughages are fed. Moreover, spectrographic analysis indicated that the greatest response was obtained from ashes characterised by a relatively high content of Mo and low Cu (40). The mode of action of the Mo is now known, but De Renzo *et al.* (41) pointed out that Mo is a cofactor for liver and intestinal xanthine oxidase.

### *Cobalt*

Cobalt deficiency is usually associated with vitamin-B<sub>12</sub> deficiency, a sensitive test for cobalt deficiency being the vitamin-B<sub>12</sub> activity of blood plasma (42) and of liver (43).

Because it is often not practicable to treat deficient pastures with Co salts a new technique has been developed (44) whereby a pellet of cobaltic oxide baked with china clay placed in the rumen releases amounts of Co sufficient to control cobalt deficiency.

This liberation of Co from such pellets has also been used to control Phalaris staggers, a demyelinating disorder of sheep characterised by hyperexcitability, muscular tremors and a rapid bobbing of the head. This disorder apparently arises from a toxic factor present in actively growing *Phalaris tuberosa*, a high-yielding perennial grass. Unlike the cobalt deficiency associated with 'pine', Phalaris staggers cannot be prevented by oral administration of vitamin B<sub>12</sub> or intramuscular injections of vitamin B<sub>12</sub> or cobalt but only by oral administration of cobalt (45). This suggests that orally ingested Co promotes the development in the upper part of the alimentary tract, of micro-organisms capable of detoxifying the toxic principle in *Phalaris tuberosa*. This type of disease has also been noted recently in South Africa (46).

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### VETERINARY MEDICINES (A. N. Worden, M.A., B.Sc., M.R.C.V.S., F.R.I.C.)

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#### General

A SUPPLEMENT to the *British Veterinary Codex*, the first edition of which was published in 1953, has appeared (1) and contains 89 new monographs on drugs and many amendments to existing monographs. Notable additions include piperazine preparations, a variety of materials that have or influence -adrenocortical activity, furazolidone, Nicarbazin, tetracycline, erythromycin and polymixin B. The rapidity with which new drugs are appearing is reflected by the fact that many compounds already in widespread use are not included. The appearance within the next few years of a new and greatly enlarged edition of the *Codex* itself may be anticipated.

There have been two useful textbooks, viz., Alexander's introduction to veterinary pharmacology (2) and Daykin's complete

rewriting (3) of the text first produced by Wallis Hoare and familiar in its successive editions to several generations of veterinary students.

### Anthelmintics

Phenothiazine, despite its limitations, continues to be widely used. Variations in purity may be considerable and Forsyth (4) has stated that when it falls below 70% anthelmintic efficiency against *Ostertagia* spp., *Trichostrongylus* spp., and *Chabertia ovina* is erratic or poor. There is, however, little apparent advantage in using material of a purity higher than 80%, at which level the efficiency of a 15-g. dose to sheep is 80%. Anthelmintic efficiency is inversely proportional to particle size and the measurement of specific surface area is more accurate than description of a particle size distribution related to an arbitrary figure. A minimum purity of 85% and a specific surface area of 12,000 sq. cm./g. by sedimentation analysis appear to be necessary for high anthelmintic effect. Drudge and his co-workers (5) have, however, provided further clear evidence that strain resistance on the part of *Haemonchus contortus* is an important factor also in determining the efficacy or otherwise of phenothiazine.

Roberts & Keith (6) have studied the relationship of dosing with phenothiazine to the acquired resistance by calves to *Haemonchus placei*. Although repeated use of phenothiazine may delay the development of resistance, and leave the animals with a heavier worm population than if left undosed, phenothiazine may nevertheless be used at intervals of ten days to control outbreaks. In another Australian study, Banks & Korthals (7) have found highly purified phenothiazine to be superior to bephenium hydroxynaphthoate in the treatment of emaciated young sheep infected with large numbers of worms—principally *Trichostrongylus* spp. and *Ostertagia*. Gibson's findings (8) with *T. axei* infestation have, however, proved favourable to bephenium hydroxynaphthoate. Scarnell & Rawes (9), as a result of field trials in Kent, have confirmed the value of bephenium embonate, administered at the beginning and end of May and again in mid-June, against *Nematodirus battus* and *N. filicollis* infestation in lambs and, from a comparative study of eight compounds, Gibson (10) has found only bephenium embonate to be effective and non-toxic in the treatment of *Nematodirus* spp. in sheep. Rawes & Scarnell (11) in a later paper, have claimed that bephenium hydroxynaphthoate (at 250 mg./kg. bodyweight) appears to be the most active anthelmintic against the nematodes commonly infesting unweaned spring-born lambs, a view that is supported by Gibson (12), who has subsequently reported virtually 100% efficiency against *N. battus*.

Studies on the anthelmintic properties of organo-phosphorus

compounds have been reported from a number of centres. Rick & Keith (13) have demonstrated that *OO*-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate is highly efficient against the common gastro-intestinal helminths of cattle, and their findings have received support from the studies on *Ostertagia* spp. of Banks and his colleagues (14), while Dunsmore (15) has demonstrated the activity of this material against sheep trichostrongyles. Rick & Keith (16) have subsequently reported that *OO*-dimethyl *O*-2,4,5-trichlorophenyl phosphate is highly effective against *Haemonchus placei* and *Cooperia* spp., but only of variable activity against *Oesophagostomum radiatum* at the dosage employed (5 g./100 lb. body weight). Similar findings were obtained for 3-chloro-4-methylumbelliferone *OO*-diethyl thiophosphate at 0.25 g./100 lb., and negative findings with diazinon, Dipterex and *OO*-dimethyl 2,2-dichlorovinyl phosphate (D.D.V.P.).

Baker and his colleagues (17) claimed that *O*-methyl *O*-(4-*t*-butyl-2-chlorophenyl) ethylphosphoroamidothioate ('Dowco 105') effectively controls several genera of Trichostrongyloidea in cattle, and most species of nematodes in the abomasum and small intestine of lambs, although inactive against *Fasciola hepatica*. Landram & Shaver (18) have reported similarly.

Vordrazka *et al.* (19) applied a new technique to the evaluation of cyanacethydrazide against sheep lungworms and claim considerable activity against *Dictyocaulus filaria* but not against *Protostrongylus rufescens*. Adverse reports upon the value of cyanacethydrazide have, however, been received from Enigk & Düwel (20) in Germany, from Mohi-ud-Din (21) in India and from Swanson and his co-workers (22) in Florida, while Rosenberger & Heeschen (23) claimed that the piperazine salt of the levulinic acid hydrazone of cyanacethydrazide is better tolerated than cyanacethydrazide itself and may be given to cattle in larger and more effective doses. Parker and his co-workers (24) have brought forward evidence from field trials with cattle lungworms to support the value of diethylcarbrazine.

In the continued search for fluke treatments, Boray & Pearson (25) have confirmed Hungarian work to the effect that tetrachlorodifluoroethane is highly effective against mature *Fasciola hepatica* in sheep at a dose rate of 0.15 g./lb. For the control of fascioliasis by indirect means, Gordon and his colleagues (26) have demonstrated that copper pentachlorophenate is a potent molluscicide that is clearly superior to copper sulphate.

### Anticoccidial drugs

This remains an extremely active field. Horton-Smith & Long (27) have undertaken a comparative study of sulphaquinoxaline, sulphadimidine, Nitrofuride, nitrofurazone, Nicarbazine and a mixture (Bifuran) of nitrofurazone and furazolidone, using ex-

perimental infections with *Eimeria necatrix*, *E. acervulina* and *E. maxima*. The results indicate that Nitrocarbazine, nitrofurazone and Bifuran give the best prophylaxis against *E. necatrix* and that Nitrofuride, nitrofurazone and Bifuran give good protection against established infections with this organism. Sulphaquinoxaline protects against *E. acervulina*. Sulphadimidine and nitrofurazone completely suppress or greatly reduce oöcyst production of *E. maxima*. The same workers (27b) found that imidazole-4,5-dicarbonamide (glycarbylamide) is effective in preventing heavy experimental infections with *E. tenella* and *E. necatrix* but inferior to sulphaquinoxaline in reducing the oöcyst production of *E. acervulina* when continuous treatment was started before infection with oöcysts. Ball (28a) has investigated the activity of various antibiotics against *E. tenella* and found spiramycin the most effective. The same worker (28b) showed that Nicarbazine at concentrations of 0.01% w/w or more in the food is effective in preventing, and 0.025% in treating, early (but not established) *E. tenella* infection. Arundel (29a) has shown that 3,5-dinitro-*o*-toluamide (Zalene) at levels of 0.01–0.03% in mash is more effective therapeutically in similar circumstances. Arundel (29b) also confirmed the efficiency of pyrimethamine and sulphonamide against caecal coccidiosis but finds that the combination is too toxic for use as a coccidiostat. Joyner (30a) has examined the possibility of folic acid as an antagonist to the toxicity of this combination and claims that 25 mg./kg. daily reverses the growth-inhibition caused by 0.004% pyrimethamine and 0.05% sulpha-dimidine in the food without reducing therapeutic efficiency against *E. tenella*. The best results with Zalene were obtained by administration to the chick early in the life cycle of *E. tenella* (regarded as a particularly suitable test organism) and good control may be effected by 0.01 or 0.0125% in the food, maintained for 10 days. Higher doses given for the first 5 days of the infection may induce a marked delayed mortality 4–5 days after removal of the drug (30b).

Smyth *et al.* (31) have reported that the continuous administration of 0.022% furazolidone in the food delays indefinitely the onset of sexual maturity in male turkeys and has adverse effects upon the fertility and hatchability of turkey eggs.

### Antitrypanosomal compounds

Smith (32) has reported that prothridium, the suraminates of ethidium and R.D. 2902 were all superior to quinapyramine in protecting Zebu cattle exposed to a high density of *Glossina pallidipes*, the reaction in the form of swellings in the dewlap being least severe in the case of prothridium. Lyttle (33), in confirming the potential excellent therapeutic value of prothridium, draws

attention to the readiness with which drug-resistant strains appear to follow after even one injection. Leach & El Karib (34) have obtained some evidence of toxicity in the field with prothidium bromide at 5 mg./kg. Their trials were complicated by transient infections which, however, they do not regard as of major importance in judging the merits of a particular drug. Metamidium chloride is very toxic when injected intramuscularly into West African White Fulani Zebu bulls at 10 mg./kg., but there was reasonable tolerance, combined with activity against *Trypanosoma vivax* and *T. congolense*, at 5 mg./kg. (35). Soltys (36) has shown experimentally that antibody-resistant strains of trypanosomes are less sensitive to suramin and anticyde than are antibody-sensitive strains.

Cooper (37) has produced evidence that the antitrypanosomal drug ethidium bromide appears to have activity also against so-called New Forest disease (associated with *Moraxella bovis*) when applied as an eye ointment containing 0.5% of the drug.

### Antibabesial compounds

Lucas (38) has compared favourably the activity of a new compound, 3,3'-diaminocarbanilide di-isethionate (M & B 5062A) with antibabesial drugs hitherto in use, using a test infection (*Babesia rodhaini*) in mice and *B. divergens* infection in splenectomised calves. Beveridge *et al.* (39) reported that this compound offers advantages over existing treatments for bovine redwater in the field.

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## FOOD

By MEMBERS OF THE FOOD GROUP

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FOR many years it has been the policy of the Food Group to divide the food field into seventeen sections covering the principal carbohydrates, various foods, methods of processing, preservation, hygiene and packaging, and each year in the Food Chapter to report on progress in about six of these sections. Of necessity this has meant that each section has been dealt with only at three-yearly intervals and then a good deal of the material is often rather out of date and the reviews sometimes too long. As methods of processing (such as canning, freezing, dehydration, packaging and hygiene) have advanced from the more fundamental to the applied stage it is considered that these sections can now best be covered as they apply to the various commodity foods. It has been decided, therefore, to reduce the sections to six, namely Cereal Products (including starch), Dairy Produce (including eggs, poultry and ice cream), Sugar Products (covering sugar, preserves, chocolate, sugar confectionery and non-fermented beverages), Meat, Fish, and Fruit and Vegetables, and to report important developments in these annually. Developments in canning, packaging, freezing, dehydration, preservatives, fortification, nutrition, hygiene, and the like will be covered as they relate to the individual foods. It has not been possible to put this scheme into operation completely this year but a start has been made and the chapter has four sections dealing with Cereal Products, Dairy Produce, Fish, and Fruit and Vegetables.

The Food Group has a very active Nutrition Panel and, as increasing attention is being paid to the nutritive value of processed foods, authors have been asked to write their review, where possible, with nutrition as a theme. In spite of all the basic research that has been carried out we are still amazingly ignorant of the nutritive changes which occur in food during processing and of the possible effect of food additives on nutritive value. It is perhaps because of this that the purity and wholesomeness of food is still the subject of much emotional thinking; even among food experts there is a surprising number who frequently appear to adopt an

attitude of prejudice rather than impartiality. In 1959 the Food Standards Committee published proposals for new controls over soft drinks which drew forth strong criticism from the Food Manufacturers' Federation and the *Lancet*, which suggested that the advice of the Committee on Medical and Nutritional Aspects of Food Policy in regard to glucose 'derived from work published many years ago . . . not specifically designed to solve the present problem', recent work by Chain and others indicating that the concept of dietary carbohydrate only supplying calories must be discarded.

There is, in this country, an abundance and great variety of food of high quality and nutritional value, and by patronising all departments of a modern food store we can easily supply our nutritional needs. Persistent campaigns are being carried out, however, to undermine public confidence in the nutritional value of staple foods by the activities of food faddists and by many misleading advertisements. This grew to such an extent in America that the U.S. Department of Health, Education and Welfare considered it necessary in July 1958 to issue an official leaflet, 'Food Facts vs. Food Fallacies'. The report of the Food Standards Committee on Bread and Flour, published this year, recommends that steps be taken to prohibit advertisements making exaggerated claims for enrichment of bread or for energy-producing qualities and the Committee agrees with the Joint Nutrition Panel that no food can properly be called 'slimming', and that such claims for breads, biscuits, rusks, rolls and certain cereal breakfast foods should be banned. The danger is that today we may be too well nourished and the School Health Authorities are becoming concerned with obesity in children instead of malnutrition.

In September of this year the Pure Food Centenary celebrations were held and the theme which emerged was the need for integration of food research and food legislation with the hope that one day International Standards for pure food might be achieved. Anyone connected with the export of food will appreciate how complex the international position is concerning permitted food colours. Of 82 food colours permitted in 22 countries, only one colour is permitted in them all. In certain spheres, however, it has been possible to work on a world-wide basis, and F.A.O., starting in 1957, have formulated a 'Code of Principles concerning Milk and Milk Products' which has been accepted by some 30 governments.

Many industrial chemists concerned with export to the United States must find it very difficult, with their limited resources of assistance, to keep abreast of the food additive position there to ensure that their products conform to the regulations concerning direct and indirect additives, including substances which might migrate from plant, wrappings or containers. Suppliers of materials to the food industry are frequently quite unaware of these require-

ments and it is the food chemist's responsibility to draw his supplier's attention to any specific requirement which might apply to his material. The lists of these additive substances prepared by the British Food Manufacturing Industries' Research Association for their members are very useful.

### **CEREALS AND CEREAL PRODUCTS (J. Williams, B.Sc., Ph.D., F.R.I.C.)**

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THIS review deals mainly with the nutritional aspects of cereals (especially wheat) and products derived from them.

Work on the development of new varieties of wheat with improved functional properties and yields continues. One variety, Viking, has received mention in the popular and trade press. In work of this type, methods of assessment of functional properties during the development stages are of great value, e.g., a sedimentation test (1), which, however, has some limitations. The quality of grain is, of course, affected greatly by seasonal variations, and the weather conditions during the 1960 harvest caused considerable difficulties and in many cases unwelcome deterioration in the baking properties of native wheat.

The Food Standards Committee formed in 1947 to advise the Ministry of Agriculture, Fisheries and Food has recently published its report on bread and flour (2). In some respects it has confirmed the *status quo* but has in other ways introduced definitions of quality. The nutritional standards for flour, laid down in the Flour Order (3) with regard to the addition of calcium carbonate, vitamin B<sub>1</sub>, nicotinic acid and iron are maintained and considered adequate. The Nutritional Panel of the Committee has recommended that no addition of riboflavin or pyridoxin is necessary. A recent paper (4), in which the rôle of calcium additions in bone formation in rats fed on a lean meat diet has been demonstrated, emphasises the function that the calcium carbonate addition to flour can play, especially in the diet of older people. A list of permitted ingredients in bread is set out in the report, and specifications are given for certain speciality breads. A minimum fibre content of 0.6% on the dry weight is chosen to distinguish brown bread from white bread and levels of 16% and 22% protein respectively are cited to characterise gluten- and high-protein breads. Limits are set regarding nutritional claims and inferences for such bread. Standards are given for the content of the characteristic ingredients of milk bread and wheat germ bread.

The recognition of commercial needs for certain additives is made in the report and improvers now in use are accepted at their

present levels. The need for further investigation and long-term chronic toxicity tests is emphasised, but in the meantime a permitted list of treatments has been prescribed, with the proviso that the position is to be reviewed in 3-5 years' time. In the case of the most commonly used bleaching agent, a limit of 50 p.p.m. has been set.

The examination of the effect of some of the customary treatments on the nutritive value of flour and bread continues. Chlorine dioxide reduces the vitamin E content of flour (5, 6), white bread being considered deficient in this respect, whilst germ-enriched and wholemeal breads are satisfactory. Essential fatty acids have received prominence in recent controversies and the effect of 'normal' treatments with chlorine dioxide and chlorine have been shown (7) to be without appreciable nutritional effect. Excessive treatment leads to a loss by oxidation during storage, which may be due to the oxidation of protective factors such as tocopherols, with consequent reduction in the induction period. In other connexions it is claimed that selenium (in quantities of the order of 1 p.p.m.) has a vitamin-E-sparing action, and in this context it is interesting to note (8) that plants differ considerably in their absorption of this element from the soil: soya-beans absorb little from the soil, wheat and barley absorb some, while certain species of Compositae, Leguminosae and Cruciferae act in a highly concentrating manner.

The International Congress of Nutrition held in Washington (9) dealt extensively with sources of protein foods. The deficiencies in cereal proteins and the virtues of supplementation with amino-acids have received considerable attention. Lysine, methionine and cystine are the main limiting amino-acids (10), although others have received mention. During the milling process there is an interference with the balance of amino-acids, depending on the extraction rate. The general amino-acid distribution in proteins from wheats of different types is very similar (11), small differences being noted in the basic amino-acids lysine and arginine. The effect of wheat germ and skim milk solids when added to a diet for weanling rats has been shown to correlate with the lysine content of the diets (12). The same effect was observed when bread made from flours of different extractions was compared (13) with and without supplementation with soya meal. In a mixed diet deficiencies in one are usually corrected by others, but in underdeveloped countries where low-value diets are prevalent, amino-acid supplementation may be essential. It is considered (14) that the use of protein-rich foods is probably more economic than fortification with separate amino-acids. Groundnuts and fish flour have found use in Africa in this connection (15).

Interesting reflections on the occurrence of strontium-90 in grain and flour have been published (16). The content in flour is

lower than in fine offal and bran, and varies in different parts of the world. Australian flour has the lowest and Russian wheat and flour the highest content.

Radiation treatment of grain and flour has received further study (17). High rates of dosage damage the enzyme systems of wheat, but at the lower levels sufficient to kill insects, such damage may not be great. One main limitation to such treatment is the effect of irradiation on the flavour.

The Report on Bread and Flour (2) has accepted the necessity for improvers in flour for bread manufacture. The mechanism by which these act remains controversial, the over-all action being characterised by two distinct phases (18*a*), a rapid initial reaction and a slower secondary reaction proceeding at a constant rate. The rates of reaction in both phases increase with increasing flour concentration and decreasing pH. The baking process destroys all the residual bromate (18*b*). The interaction of thiol and disulphide groups has again been examined (19), and it is claimed that the rheological properties of dough are related to the number of intermolecular disulphide bonds and the rate at which these can interchange with thiol groups. The action of improvers can be related to the strengthening of the dough through the inhibitions of this interchange reaction and in some cases to the formation of intermolecular disulphide bonds. Bromate is preferred to iodate because of its slower action. The reported discovery of thioctic acid in flour doughs (20) brings another factor into this complicated system.

The Preservatives Sub-Committee in its report (21) recognised that there is a case for the use of an anti-mould agent in bread, because of the increased manufacture of wrapped and sliced bread. Propionic acid or its calcium or sodium salts in amounts up to 0.3% of the weight of flour is therefore permitted, in addition to the established use of acetic acid or calcium acid phosphate as control measures against rope organisms. Other preservatives such as diacetic acid and its salts, which are allowed in the U.S.A. and Canada, are not accepted owing to health hazards. Sorbic acid and its salts are permitted in cakes (2).

Enzyme preparations are also permitted in bread manufacture to correct natural deficiencies in the flour. Treatment of biscuit flours is also mentioned and a recent patent (22) employs a proteinase in admixture with glutathione, cystine and cysteine or their salts to modify the gluten properties as the occasion demands.

With the modern pattern of food distribution, measures to prolong the life of the article are of interest. In baking, a number of such adjuncts have been recommended and new emulsifying agents and so-called 'crumb softeners' find their individual supporters. In this country, as in others, freedom from health hazards is an essential, and where there is any doubt, a bar is placed on the use

of the particular substance (12, 23). The use of super-glycerinated fats, stearyl tartrate and lecithin is permitted.

The proportion of bread which is sold wrapped and sliced continues to increase. A wrapper is called upon to fulfil the two main functions of protecting the contents and at the same time displaying the bread. Waxed paper still remains the most popular protective wrapping material for bread, but increasing attention is being paid to transparent plastic materials. Various types of Cellophane have found favour and, after the technical difficulties of sealing had been overcome, polyethylene films have been used extensively. Polypropylene has mechanical advantages, giving clear visibility, adequate stiffness for machine wrapping with a soft feel, and providing satisfactory protection for the bread. The introduction of these latter films calls for close attention to practical details in all spheres. The move towards bulk handling and storage of flour and other raw materials used in the bakery continues to gain ground, with consequent benefits in hygiene. The Food Hygiene Regulations (24) have extended the precautions and provisions recommended for those premises responsible for the preparation of food in England and Wales and its subsequent handling.

On the technological side, there have been no outstanding developments of value in the milling of flour or the production of new cereal products of nutritional value. The investigation of the applications of air classification continues and classifiers are available in which flour is separated into fractions of differing particle size by means of selective air currents. Such separations lead to fractions of different protein contents with consequent different fundamental flour properties and the general emphasis has been on commercial uses (25). The studies have been extended to cover flour from differing types of wheat. Much of the work is being carried out by individual interested concerns and the results have, consequently, a restricted publication. During air classification there is a displacement of B-vitamins accompanying the displacement of proteins (26). Finely ground portions of scutellum and aleurone layer which are concentrated sources of these vitamins are segregated into the finer high-protein fractions.

In bakeries, continued interest has been shown in the development of continuous process and in the mechanical development of dough. There are a number of processes which have been put forward using a pre-ferment followed by mechanical development of the desired physical properties in the dough (27). The energy requirements for satisfactory bread production by such a process have been studied (28). An attempt has been made to assess the proportion of this energy which is associated with breakage of disulphide linkages in the dough—the linkages considered earlier in connexion with improver action—and the experiments have

demonstrated the significance of this linkage. Gas-liquid chromatography has been used to investigate flavour development during fermentation and baking (29) and many compounds have been detected. Synthesis from such results is, however, often disappointing.

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## DAIRY PRODUCTS (J. G. Davis, Ph.D., D.Sc., M.I.Biol.)

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DURING the past two years the subjects which have been of special interest in the field of dairy science and technology have included the composition of milk, especially in relation to quality payment, rapid methods for the determination of proteins in milk, the nutritive value of milk products, milk fat in relation to atherosclerosis and thrombosis, bulk milk collection and handling, and new methods and equipment for sterilising milk

### The composition of milk, especially in relation to quality payment

The most important publication on this subject during the last few years has been the report of the Cook Committee on milk



composition in the United Kingdom (*1*). Since this year (1960) was the centenary of the first act concerned with the prevention of the adulteration of food, it is especially opportune to review the question of the purity and composition of milk, particularly from the point of view of the consumer. Before about 1900 nearly all milk was sold direct from the herd, or even the cow, to the consumer. Hygiene did not exist in the modern sense, and adulteration was not only universal but an accepted practice in the dairy trade. So little was understood at this time of the factors controlling the compositional quality of milk that the Wenlock Committee in 1901 recommended presumptive minimum standards of 3% fat and 8.5% solids not fat (S.N.F.) (*2*). This legal basis has controlled the sale of milk in this country for the last 60 years.

During this same period the method of milk distribution and our scientific knowledge of milk quality and its control have both undergone revolutions. Practically all milk today is bulked, pasteurised or sterilised and sold by big firms. In England and Wales only 5% is sold by producer-retailers (12% in Scotland and 3% in Northern Ireland). Thanks to the efforts of the public analysts and the dairy scientists, watering of milk is now rare and milk as sold to the public is usually of almost constant composition.

About three-quarters of the milk produced in England and Wales is consumed liquid (Scotland 60%, Northern Ireland 35%), so that on a quantity basis the ordinary consumer is more important than the manufacturer of milk products. Possibly for this reason the interest in the chemical quality of milk has centred almost entirely on the fat content, and 'cream line' has usually been the biggest selling factor in the milk trade, some dairymen considering that a good cream line is even more important than keeping quality. The S.N.F. content has not only been ignored by the consumer but has not even been understood. Nutritionists have for some time been emphasising its greater importance, and it is gratifying to note that the Cook Report has been particularly concerned with this aspect.

Two distinct problems have been considered in this report, firstly how to prevent the decline and raise the compositional standard of milk in relation to S.N.F., and secondly what quality-payment system, if any, would be best in the interests of all concerned— the producer, the liquid milk distributor, the manufacturer and the consumer.

We now have a considerable amount of information about the variations in the fat and S.N.F. contents of milk and the reasons for them. Breed is undoubtedly the most important factor. The milk from the Friesian cow is on average the poorest in both fat and S.N.F.; 30 years ago it was in a minority in the herds of this country, but today is at least as numerous as the Shorthorn which earlier constituted 70% of our dairy cows, and is likely to increase steadily in numbers during the next few years.

There are well-recognised seasonal variations covering a range of 0.4% fat and 0.3% S.N.F., but there is a fairly standard pattern throughout the year and little can be done to even out these seasonal variations.

Until recently the effect of method of feeding the cow on the composition of its milk was but ill-understood, and the evidence on the subject was very confusing (3-5). As a result of work carried out at the British Dairy Research Institutes, much more precise knowledge of the effect of feed is now available. Possibly the most important finding is the realisation that prolonged feeding of a food low in energy value will lead to a lowering of the S.N.F. content of the milk (6-8). This effect may not be immediately apparent, but it can be very persistent, and the longer the period of underfeeding the more persistent it will be. Both the war and the development of modern methods of feeding, e.g., silage, may be responsible factors, because many farmers were unable to obtain sufficient high-energy foods for their cows or had no precise knowledge of the quality of the hay, silage, etc., which they were feeding. There is little doubt that continued efficient feeding will not only bring about an increase in yield, but will improve the S.N.F. content if this has been low. It has been calculated that under these circumstances it would cost about 1d. per gallon to increase the S.N.F. value by 0.1%.

Breeding is a third factor whose importance is now becoming realised by most milk producers. The purchase of milk on a quantity basis for many years has undoubtedly made the farmer 'gallon conscious', and has furthered the increase in the number of Friesian cows and encouraged the farmer to ignore quality aspects. It is now recognised that while, broadly speaking, fat and S.N.F. vary together, animals can differ in the fat and S.N.F. characteristics which they transmit to their progeny. It has been contended that as there is a correlation between fat and S.N.F. values, it is sufficient to pay attention only to fat values, but this is a short-sighted policy and the Cook Committee places emphasis on the importance of considering S.N.F. aspects in their own right. Unfortunately, any improvement in the S.N.F. value of the country's milk could only be altered very gradually by attention to breeding. The report suggests that an improvement from this source would amount to only about 0.02% S.N.F. per annum.

A fourth major factor is mastitis. Before the penicillin era about 35% of our cows were suffering from sub-clinical mastitis, mainly due to *Str. agalactiae*. Antibiotics have largely eliminated this particular type, but other types have become more prevalent and it is probable that 15% of our dairy cows have the disease in one form or other today. The sub-clinical forms may not affect the fat and protein contents to any extent, but they lower the lactose and increase the salt content. The overall effect of mastitis on the

national milk supply is probably not significant, but in individual herds it may easily be responsible for bad failures on S.N.F. tests.

One method of ensuring that the consumer receives a milk of known chemical quality is to standardise it, by adjusting the fat content to an arbitrary value, e.g. 3%. If this were done the general milk supply would be poorer in fat (at present it averages about 3.7%) but the consumer would get an article of known and constant fat content. Standardisation would almost certainly lead to homogenisation, as is the usual practice in Europe and elsewhere. This has the advantage of making the milk more creamy for a given fat content, but homogenised milk readily develops a certain type of taint which is difficult to avoid. There appears to be little enthusiasm in this country for such a revolutionary practice.

It has long been recognised that the legal presumptive minimum standards are unsatisfactory for those whose responsibility it is to prevent the adulteration of milk. A further difficulty arises from the fact that the fat content of milk can easily be adjusted by the simple process of allowing part of the fat to rise to the surface. The normal control method of the public analyst is to test milk samples for fat and S.N.F., and, if one or both values are below the presumptive standards, to apply a freezing point test. Since this is easily the most accurate method for detecting added water, it is strange that in the rest of Europe other methods are still employed for detecting adulteration. The Cook Committee comes to the conclusion that there is no reason for retaining a legal presumptive minimum standard for S.N.F., but it considers the possibilities of fixing an absolute standard, which would have to be lower than 8.5%, because of low values in late winter; it was decided that an absolute standard is not practicable at the present time. Somewhat surprisingly, the retention of the presumptive standard for fat at 3% is favoured without convincing reasons, and it is suggested that it may be possible to institute such an absolute standard within the next 5 years, and one of 8.5% S.N.F. within the next 10 years.

The report also comments on the desirability of having a satisfactory legal definition of milk and suggests the following:

'Cows' milk means the secretion, excluding colostrum, which can be gained by normal milking methods, from the lactating mammary gland of the healthy, normally fed cow.'

The Committee also recommends that it should be made a specific legal offence to abstract fat from milk intended for sale as such, and also that the evidence of the freezing point test should be accepted in a court of law as proof of the presence or absence of added water. Naturally the seller would be entitled to have evidence offered by his own analyst.

The report gives detailed consideration to various quality payment schemes which have been suggested from time to time. There

are clearly many difficulties in applying the ideal scheme under which the fat and S.N.F. values of all producers' milks would be determined at frequent intervals, and payment made directly on a basis of these results. The cost of such a scheme applied to every producer in the United Kingdom would be very high, and that suggested is really a toned-down modification of the ideal scheme, although it can be approved for the emphasis it gives to S.N.F. values.

The main recommendations of the report are summarised under 19 headings. The Committee recommends that milk should continue to be sold as it comes from the cow (except for special grades), and that both fat and S.N.F. values should continue to be the criteria for legal and marketing purposes. Differential payment schemes for S.N.F. should be introduced as soon as possible in the United Kingdom and these should take the form of penalties where it is not possible to institute a full range payment scheme. In Great Britain penalties should be imposed when the S.N.F. value falls to 8.4% or lower.

A particularly interesting recommendation is that the terms of reference of the Joint Milk Quality Control Committee should be extended and among its duties should be the task of keeping the Minister informed of developments affecting milk composition and giving advice.

For general discussions of the background to quality payment schemes see reference (9).

Some very useful publications giving general information about the British dairy industry have been published during the period under review. Crossley (10) has written a book on the occasion of the 15th International Dairy Congress. Strauss (11) has given a comprehensive analysis of the structure of the dairy industry in England and Wales, and the Milk Marketing Board, in addition to its two annual reports, has issued a booklet of dairy facts and figures (12). The usual detailed statistics for agricultural production have been published by the Ministry (13).

### Composition of milk in other countries

In South Africa, Bakalor (14) has published detailed analyses of milk in that country and discussed the possible reasons for variations. He recommends that all milk should be bought on a quality basis. In the Netherlands (15) comprehensive schedules have been issued privately giving detailed chemical analysis of the milk of selected cows over 7 years, and further information of this nature is to be published. In the U.S.A. bulk milk analyses have been given by Nickerson (16), and daily variations in the composition of herd samples have been studied by Mickle (17), who issued a warning about the danger of relying on correlations

between constituents. A similar study of variations on individual cow samples has also been published by Fricker (18).

Studies of the effect of various factors on the fat and S.N.F. values of milk have been made in England (19), in Wales (20) and in the U.S.A. (21). The last two papers discuss the possible influence of mastitis, which is still a very controversial subject.

Considerable interest has been taken recently in genetic influences on the composition of milk. Krosigk (22) has given correlations between a number of factors and fat, protein, S.N.F. and total solids, and (23) obtained genetic correlations of 0.70 between fat and protein, 0.55 between fat and S.N.F., and 0.92 between protein and S.N.F.

The effects of a number of genetic and environmental factors on the S.N.F. value have been investigated by Wilcox *et al.* (24), and Comberg & Voigtländer (25) have studied the effect of feeding and management on various constituents. They agree with other workers that although fat, S.N.F. and proteins are positively correlated, it is not possible to assess S.N.F. or protein content from the fat value.

There has been increasing interest in the nutritional value of the protein in milk during the last 3 years. Fluctuations in the protein content of milk, and the reasons for them, have been studied (26), and the protein content examined from the point of view of the effect of mastitis (27). It is concluded that mastitis milk generally contains less protein. It has long been known that casein is depressed and globulin increased, and the change in the albumin globulin ratio is considered to give the best indication of abnormality.

### Quality payment

In those countries in which quality payment schemes are in force, fat is the usual constituent for the basis of payment, although it would seem preferable from most points of view to base it on total solids, or at least on fat plus protein (*cf.* 9*b*). In Holland, where most of the milk is manufactured, it is now realised that the correlation between fat and protein is not good enough to justify payment on the fat value alone, and milk is now bought on both fat and protein contents. For this purpose protein is estimated by the Kofranyi method (distillation of ammonia from milk in the presence of alkali), which is considered sufficiently accurate for the purpose (28). In Italy, Guccioli (29) discusses quality payment, and especially the methods for assessing protein content, and considers the Kofranyi method to be superior to the formol titration method. An account of the Dutch method and a considerable amount of data on the subject are given by Lolkema (30).

*Determination of protein content*

The interest in the protein value of milk has resulted in the publication of many papers on simplified methods for determination of protein in milk. The Kjeldahl method is normally used for reference purposes, and the most popular simple methods are the formol titration (used by Walker for casein measurement), the Kofranyi method and various dye-absorption methods. In general all workers (31) agree that, taken over a number of samples, the formol titration value is sufficiently accurate for the purpose. Various workers prefer different methods for the formol titration but these are all basically the same and it is unlikely that differences between them would be of significance for a number of results. There appears to be general agreement that the Kjeldahl and Kofranyi methods give virtually identical results (32).

Ingenuous methods have been described by Konev & Kozunin (33), using the relationship between protein content and fluorescence. Agreement with the Kjeldahl method was claimed to be  $\pm 0.17\%$ , with an average error of  $0.08\%$ . The classical xanthoproteic reaction between protein and nitric acid has been revived (34), the colour being measured with a blue filter after neutralisation; the sensitivity is claimed to be in the range  $0.5$ – $5$  mg. protein.

One of the most rapid methods to attract attention in the last 2 years is that based upon the precipitation of the protein in milk by certain dyes. The excess dye remains in solution and can then be estimated by the usual methods. With Orange G, Treece (35) obtained values of  $3.2456 \pm 0.0394\%$ , and  $3.2475 \pm 0.0193\%$  by the Kjeldahl and dye methods respectively. It is evident that the accuracy is quite adequate for payment purposes. Similar data for the accuracy of the Orange G method have been given by Ashworth (36) and (for serum proteins) by Seals & Ashworth (37). Shiga *et al.* (38) compared Orange G with Amido-black 10B, and found the latter to be superior. Their results showed a standard deviation of  $0.083\%$  from the Kjeldahl method. Other workers confirmed that the Amido-black method is probably the best (39). The necessary conditions for avoiding the errors associated with methods of this character, and detailed instructions for carrying out the tests accurately and quickly have been given.

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### Bulk milk collection and handling

It is obvious that any system whereby milk can be handled in bulk from the farm to the collecting depot will appreciably reduce handling costs. There has been considerable interest during the last few years in the system of bulk farm collection, in which the milk from the cows is passed directly into a refrigerated tank on the farm, and thence is pumped to a tanker which takes it to the collecting depot. A specification for a bulk farm tank has been

issued in the United Kingdom (1), and a test report (2) shows that such a tank can cool 175 gallons of milk per day from 90°F to 40°F or lower. The insulation of such a tank is an important feature (3). The system is possibly only suitable in flat areas, but is being developed in many other countries, particularly in the U.S.A. and also in Russia (4). Accounts of the progress made in this system have been published in Scotland (5), Canada (6), New Zealand (7), U.S.A. (8), Austria (9) and Sweden (10).

All those familiar with the bacteriological aspects of milk collection will realise the potential dangers of such a scheme of collection. Contamination and deterioration of milk in a single 10-gallon churn is of limited importance, but spoilage of hundreds or thousands of gallons of milk is a very serious matter. Studies of the bacteriological quality of milk collected by this new system have been published (11). As with the classical method of milk collection, cleanliness and sterility of utensils and the temperature of holding milk are factors of outstanding importance in the production of a milk of satisfactory bacteriological quality. Provided that efficient methods for cleaning and sterilising all the farm equipment which comes into contact with the milk are used, this system can be operated satisfactorily. Some interesting differences in the proportions of failures on colony count, presumptive coliforms, and psychrophilic organism counts have been reported, and these are doubtless due to the different conditions, particularly in respect of the fact that all the milk is bulked at the farm. The results of controlled schemes have been published in U.S.A., where preliminary incubation of the samples for 18 hours at 55°F, has been found useful (12). The relation between colony counts and dye reduction time may be different on account of the low reducing ability of the higher proportion of psychrophilic and thermoduric organisms in such milk (13). Other bacteriological data have been given in Canada (14), U.S.A. (15) and in Germany (16). Broadly speaking all workers come to the conclusion that, if properly carried out, this method can give milk of high bacteriological quality, although a slight modification in bacteriological testing is desirable. Some workers (17) have found a high proportion of samples with excessive sediment. Although such a position is unsatisfactory, it must be borne in mind that there is no necessary correlation between the results of sediment and bacteriological tests.

Few data on costings are available in the British literature, but a number of publications in U.S.A. (18) deal in some detail with the economic aspects of bulk collection compared with can transport. Costs for capital outlay and assembly have been given by Kelley (19) and Seale (20). An interesting aspect has been discussed by Ahrens (21), who has used the heat-pump idea to utilise the heat extracted from the milk during cooling in the farm bulk tank.



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**Sterilised milk**

About 95% of all milk consumed in England and Wales is heat-treated and of this about 12% is sterilised, and the proportion is increasing steadily. Scientifically the main interest has been the application of quick sterilisation or ultra-high-temperature methods (UHT) which involve heating milk to a temperature of about 140° for about 2 seconds. It is almost impossible to measure accurately the holding time in this process. Quick sterilisation permits a less drastic heating of the milk in the bottle, and shows the way towards aseptic filling, which appears to be the ultimate objective in the dairy industry (for general description of the sterilising process and equipment see references 1, 2).

The methods and plants used in other countries have been described by various authors (3).

In Holland, Labots *et al.* (4) consider that the main sources of contamination by spores are the equipment between the steriliser

and the bottle and the air, bottles and closures do not appear to be important. Hints on flavour control are given by Cogdill (5) and the conditions controlling pressure build-up in bottles during sterilising have been studied (6).

Three main types of equipment have been developed for quick sterilisation: tubular heaters, plate heat exchangers, and steam injection equipment (7). Lelièvre (8) deals in some detail with uperisation, as developed in Switzerland, and the French method developed by Laguilharré (9). Similar systems are in use in Denmark (10) and Germany (11). A fundamental study of milk sterilisation by steam injection methods has been made by Kaliba *et al.* (12). Advances have also been made with in-bottle sterilising equipment, e.g., a very neat unit suitable for small dairies (13), continuous (14) and semi-continuous systems (15).

One of the main problems in the development of quick sterilisation methods has been the testing of performance. Laboratory and small-scale models can give useful information but especial care is necessary to ensure that the conditions are made as near as possible to those in the production equipment. Apparatus for this purpose has been described (16). The results of performance tests with a plate heat exchanger have been given by Humbert *et al.* (17), who obtained a holding time of 5 seconds at 280°F. Milk receiving this treatment was sterile.

Laboratory controlled experiments devised to determine the time-temperature conditions necessary to achieve a 99.99999% destruction of spores have been described by Franklin *et al.* (18). Their work indicated that a temperature of 130.5°C was necessary with milk, but 135°C with water. These authors have also published thermal death curves (19). Similar fundamental studies with heat-resistant spores have been described by Burton and his colleagues (20).

It is evident that any methods which are purely physical or mechanical in nature are to be preferred to those, such as heat treatment, which can affect the organoleptic and nutritional properties of milk. It is possible by ultracentrifugal methods to remove a high percentage of the micro-organisms in milk (21), and it has been claimed that by a suitable design as many as 99.5% of the bacteria can be removed in this way. The method is basically the same as the clarifier, which has been in use for many years for the purpose of avoiding sediment in sterilised milk. With the development of sterilisation as a process, the ultracentrifugation of milk may come to be recognised as a standard method of treatment.

It is acknowledged (22) that sterilisation does more damage to milk than any of the other ordinary processes. There appears to be little effect on the lactose (23), but some destruction of vitamin B<sub>1</sub> occurs (24). Steam injection methods have a homogenising effect (25). Milk treated by the UHT and in-bottle processes suffers some

loss in the biological value of the protein, although the true digestibility is not significantly altered (26). There may be a 10% loss in lysine (27) and a slight loss in riboflavin (28). The effect of sterilisation on vitamin B<sub>6</sub> has been discussed by Bernhart *et al.* (29), and on the availability of calcium by Henry & Toothill (30).

The numbers and types of spore-forming bacteria which survive in commercially sterilised milk have been studied by Grosso & Bergamino (31), and by Hermier & Bergere (32). The latter authors found that nisin could be used to prevent vegetative multiplication and also to reduce heat resistance of spores. The types surviving have also been described by Ridgway (33) and Galesloot & Labots (34). The latter authors suggest that it is better to incubate bottles at 30°C for 5 days rather than at 37°C for 3 days in sterility control tests. The factors controlling spore germination have been studied by Taylor (35) and the causes of carbolic flavour in sterilised milk investigated by Labots & Galesloos (36). This defect may be enhanced by contamination with *B. circulans* derived from infected bottles and surviving in the detergent solution in the bottle washer.

Obviously the most efficient method of sterilising becomes useless unless the sterile milk can be packed in such a way as to maintain its sterility. The most common practice is to use bottles with crown corks and similar closures (37), and a series of papers in Denmark has compared packaging in bottles and in cartons (38). The ingenious Tetra-Pak has also been used for the aseptic filling of sterilised milk (39), and this problem is unquestionably one of the most interesting and the most important in the dairy industry at the present time. It appears unlikely that the main disadvantages of bottles for milk (weight and fragility) will ever be eliminated, and it is probable that if any carton system can be both efficient and compete economically with the bottle, then it will rapidly become universally adopted.

Although there has been much interest in aseptic filling into bottles or cans it does not appear that much progress has been made. Methods have been suggested (40) but no dairy company appears to have sufficient confidence in any one of these to abandon the existing classical method, i.e., sterilisation in bottle with or without preliminary quick sterilisation. Nevertheless, there can be little doubt that it is only a matter of time before a successful method is evolved. If an intermediate stage of long-keeping pasteurised milk were considered by the industry and the consumer, a suitable objective would be a failure of not more than 3 in 10,000 containers. For example, this would allow one contaminated from the milk itself, one from the container and one from the equipment or air. Even if sterility in the strict bacteriological sense were not obtained, such a system might permit delivery every second or third day and so help towards the solution

of what is probably the most important economic problem in the dairy industry, namely, how to obtain a five-day week.

A few papers have been published on special types of sterilised milks and milk products. Sterile concentrated milk still attracts attention in the U.S.A. (41). In the United Kingdom, the only special product of any consumer interest is chocolate milk, a method for making which has been described by Hansen (42). Various types of reinforced milks have been described (43).

Laboratory control methods are given by Tentoni (44) and other authors (45). It may be emphasised that ordinary bacteriological methods are quite useless for sterilised milk. Incubation of the bottles at 20, 37 and 55°C is the only sound method, or, for a restricted controlled system, 37°C is the best single temperature.

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## FRUIT AND VEGETABLES (J. C. Fidler, O.B.E., B.Sc., Ph.D., M.Inst.R.)

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A BOOKLET published late in 1959 by the International Institute of Refrigeration (1) lists the conditions which have been internationally agreed as most suitable for the storage of fruits and vegetables; this should replace many existing publications, which are often unreliable.

Fidler (2) lists the conditions applicable to apples and pears. For pears there is a marked trend towards the use of lower temperatures (delivery of air at 29°F) in air, but for apples gas storage is generally most suitable, and atmospheres free from carbon dioxide and with very low (about 2%) oxygen may prove useful. Tomkins (3a) has described results obtained by a small-scale method of testing different gas mixtures, and has recently (3b) discussed current problems in research on gas storage. All methods of gas storage in which the sum of oxygen and carbon dioxide concentrations total less than 20% involve the use of a 'scrubber', to remove carbon dioxide. Mann (4), in a paper giving technical data on construction of refrigerated gas stores, discusses the efficiency of a new system of scrubbing (5) with dry hydrated lime.

Gas storage is now widely adopted in the U.S.A., where it is known as C.A. (controlled atmosphere) storage. Many American stores rely on the solubility of  $\text{CO}_2$  in water for scrubbing. The operation of such a scrubber (developed by Dewey *et al.*, 1957) has been analysed (6), and the efficiency shown to depend primarily on the method of aeration of the water, external to the store.

Gas storage is not used commercially for the storage of fruits other than apples and pears, but there is no doubt that it could be used for many other tissues. For example, Couey (7) has shown its suitability (7%  $\text{CO}_2$ , 7%  $\text{O}_2$ ) in the storage of Eldorado plums.

Californian practice in handling and storage of grapes is described in an article (8) which contains much valuable information on packaging, prevention of decay, and practical application of the method of forecasting decay developed by Harvey (see below).

Although gas-storage normally means storage in an atmosphere modified by the respiration of the produce, the effects obtained may be induced by artificial addition of gases. Thus Smith (9) describes the use of high concentrations (20-25%) of carbon dioxide in the transport of raspberries, and storage of blackcurrants for a month at 2°C in 50%  $\text{CO}_2$  (plus air) for one week, followed by 25% for the remainder of the period. This process is now used for storage of blackcurrants for processing into juice.

Gas-storage effects can also be produced without using specially built stores. By enclosing fruits or vegetables in films permeable to oxygen and carbon dioxide, with appropriate film thicknesses (or by suitably perforating the films) and ratio of weight of produce to area of film, it is possible to arrive at atmospheres with lower concentrations of oxygen and higher concentrations of carbon dioxide than in air. This has been applied to apples (10), pears (10, 11), and chestnuts (12). Eaves (13) has constructed a jacketed gas store from Mylar plastic sheets.

'Consumer' pre-packages of fruits and vegetables are small-scale applications of the above procedures; they are fraught with dangers arising from unsuitable internal atmospheric conditions. Tomkins (14) and Hardenburg (15) have both discussed the pre-packaging of produce, with reference to control of gas composition, and biological effects.

Pre-packaging has brought with it many new products and new problems. One new product is the peeled (and often chipped) potato; the problem is to avoid browning of the tissue, which may be done by sulphite or by reduction of oxygen (16). Depletion of oxygen, by use of an impermeable film (Cryovac, polyethylene), led to formation of alcohol, and had to be used in conjunction with refrigeration to reduce the incidence of off-flavours. It is known that some vegetable tissues will tolerate freezing, if the temperature is not too low and the time of freezing not too long, but much more

work is necessary. Thus the observations of Boyes & Ginsburg (17) on the tolerance of deciduous fruits to temperatures of 24°F and 20°F are timely. Stone fruits are very sensitive and are quickly injured; grapes will tolerate these temperatures for 12–24 hours, but pears vary in sensitivity according to variety, Bon Chrétien being very sensitive.

During the past four years much work has been done, in New Zealand and in the U.S.A., on the use of bulk containers (which hold 15–25 standard bushel boxes of fruit) for harvesting and storage of fruits. Such containers not only reduce labour requirements, but also largely eliminate bruising. Much ingenuity is shown in methods of emptying the bins, e.g., by water flotation (18). De Beaux (19) has commented on Australian experience with large containers for apples sent by sea to the U.K. Refrigerated transport of perishable foodstuffs is a form of storage; special conditions, of construction and of use, are demanded according to type of produce, duration of the journey, and mode of transport, whether by rail, sea or air (20).

Certain produce from some regions may not require stringent conditions to ensure arrival in good condition. It has been shown (21) that oranges can be carried successfully from South Africa at 13°C, instead of the more usual 4°C. The journeys were made in ordinary cargo vessels, insulated with light-weight disposable foil, and cooled by portable refrigeration units. Very considerable advantages in cost and use of cargo space accrue from such methods.

Much less is now heard than 4 or 5 years ago about the role of volatile constituents of respiratory gases from plant tissue. This is partly because the questions have been simplified by finding that physiological activity is negligible at low temperatures, yet it is more complicated as more is known about their nature but no more about their origins. This work has been facilitated by developments in gas chromatography (see Meigh (22)). As an example of sensitivity, the lower limit for ethylene is now about 0.03  $\mu$ l. of ethylene in 1 litre of air, using a 1-ml. sample. It is of interest that the results obtained for production of ethylene by apples confirm results obtained 12 years ago by Fidler by purely chemical methods.

Volatile substances may be added as aids to storage. An important series of articles on storage and handling of potatoes, by Burton (23a), describes, *inter alia*, the use of nonyl alcohol as a sprout suppressant. In a further article (23b) the same author compares the cost per ton of potatoes treated with different chemicals, as sprays, dusts or vapours, nonyl alcohol being cheapest. Burton & de Jong (24) have reviewed work on suppression of sprouting of potatoes by  $\gamma$ -irradiation; 10,000 rads or less are sufficient and technically feasible, although not on individual farms. However, irradiation accelerates sweetening and breakdown, and may increase rotting.

Much less work is done on vegetables than on fruits, but Parsons (25) has re-investigated the storage of celery, for which 32°F is the optimum temperature, quality being maintained longest in crates lined with polyethylene film.

The quality of many vegetables depends on rapid cooling and maintenance of low temperatures. This is especially important for produce, the flavour of which depends on sugar content and which has high rates of respiration, e.g., sweet corn and peas. Stewart & Barger (26) found that the method of cooling was unimportant for peas, but that hydrocooling was most effective with sweet corn; both vegetables benefited greatly from top-icing during transport.

In the field of plant physiology, it had long been thought that citrus fruits did not show the 'climacteric peak' in the respiratory activity found with many fruits, but Trout *et al.* (27) claim to have demonstrated recently its occurrence in Australian-grown oranges. In many fruits the climacteric is closely correlated with senescent changes, but this is not necessarily so for the orange.

The olive fruit, though very important commercially, has received little attention from the physiologists. Now Maxie *et al.* (28) have investigated the respiration and ripening of olives, and the effects of temperature, ethylene and 2,4 D.

As might have been expected, radio-tracer techniques have been adopted enthusiastically. McCollum & Skok (29) fed  $^{32}\text{P}$  and  $^{14}\text{C}$  compounds to tomatoes, to investigate translocation of nutrients into the fruit. It was shown that most of the nutrients have entered the fruit when pink coloration begins to appear.

Research on phenolic constituents of plant tissue being fashionable and certain of these being known to be fungistatic, it is not surprising that attempts have been made to relate naturally occurring phenolics with resistance to fungal attack. Hulme & Edney (30) have shown that chlorogenic acid may inhibit the germination of *Gloeosporium perennans* in culture, but that the overall concentration in the peel of apples seems to be too low to be effective. Variation in susceptibility to rotting is not accompanied by corresponding variations of gross content of phenolics.

For certain fungal diseases of fruits it is possible to forecast the extent of decay during refrigerated storage, and thus to market the fruit before rotting can become serious. The method, which depends on rapid appearance of decay at a fairly high temperature, has been used successfully for prediction of rotting by *Botrytis cinerea* on grapes, and by *Gloeosporium perennans* on apples (31).

Leaf spot disease of bananas (*Mycosphaerella musicola*) not only greatly reduces the yield of fruit, but is reputed to lead to production of bananas which ripen excessively quickly, so that they cannot be transported successfully. The disease has only recently yielded to treatment, low-volume spraying with oil being effective (32).

A comprehensive book on the banana, including its chemistry,



physiology, and storage properties, has been published by Simmonds (33).

Physiological or functional diseases of plant tissue continue to receive attention. Treccani's book (34) on the cause and prevention of physiological diseases of apple fruits is one of the best to have been published to date and is well illustrated.

Superficial scald of apples is probably the disease on which most work has been done. Fidler (35) has reviewed the available information on control of this disease; much of the evidence is conflicting, but while much can be done to control scald by orchard and storage management, chemical methods hold most promise. The best so far is diphenylamine (not yet released for use) (36). Harvey & Clark (37) described a method of estimation of diphenylamine residues on apples, and the effect of different treatments.

Bitter pit of apples may occur either in the orchard or during storage, and causes serious losses in some districts. Until recently, no good measure of control was known, but Martin *et al.* (38) have shown that spraying the trees with solutions of calcium acetate or nitrate reduces the incidence of bitter pit. Similar results have been obtained by Askew (39) and Baxter (40).

The mineral nutrition of the tree thus has an important bearing on the storage behaviour of the fruit. The results of a complex series of experiments on this subject have been published by Tiller *et al.* (41), who discuss the influence of N, P and K on yield, storage properties and development of fungal and physiological injuries of apples.

All the foregoing relates to fresh produce, i.e., in the living state. There have been no advances in frozen food technology in the past year; indeed, there are signs that many people are worried about lack of standards, especially international standards, both of quality and of definitions. These, and similar questions, have been discussed at two refrigeration congresses in the past year (42).

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**FISH AND FISH PRODUCTS** (G. Hobbs, B.Sc., Ph.D.,  
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### Chilling

SINCE 1955 work on the effects of handling and stowage procedures on the quality of fish has continued (1, 2), the most important

feature of the results being emphasis on the fact that rise in temperature of the fish at any point results in accelerated spoilage.

Use of refrigerated brine for preservation of fish both at sea and on land has spread rapidly over the past few years (3). The relative merits have been discussed (4) and the chemical and physical changes occurring in fish stored in this manner have been studied (5). An extension of storage life over that with normal icing has been claimed for halibut and salmon (6) but not for cod and haddock (2).

By use of ice made from sea water, lower temperatures are achieved (although partial freezing is liable to occur) (7-10). It is claimed that selachian fish have a lower freezing point than teleosts, and hence do not freeze in sea water ice (10). In spite of partial freezing, no differences could be detected after cooking between the flavours and textures of fish kept in sea water ice or in fresh water ice (7, 9).

Work on the chemical composition of fish has been reviewed recently (11), and chemical changes occurring during storage in ice have been described (12).

For the objective assessment of quality of fresh fish, estimation of trimethylamine, total volatile bases and volatile reducing substances are still the most satisfactory tests (13). It has been claimed, however, that accumulation of ammonia is a better index of spoilage than trimethylamine (14). Other tests suggested include accumulation of indole (14), measurement of refractive index of the eye fluid (15), measurement of succinic acid dehydrogenase activity (16), and reduction of tetrazolium salts either by tissue suspensions (17), or by the bacteria on the skin (18). Trials with this last technique have shown that it is less reliable an index of spoilage than the trimethylamine value (2).

A correlation between pH and spoilage has been found for oysters (19); and measurement of rate of acid production from carbohydrate or rate of reduction of methylene blue is claimed to give an accurate assessment of the bacterial load (20). Some work has also been reported on the spoilage of squid (21) and shark meat (22).

The preservation of fish by use of additives was fully reviewed recently (23).

### **Freezing and cold storage of fish**

A difficulty in investigating the effect of different cold storage treatments has been the lack of a really satisfactory method of measuring the deteriorative changes that occur in the muscle, the most common method being determination of the solubility of the muscle in 5% sodium chloride, which decreases during cold storage. Recent papers have confirmed that there is some correlation with

taste panel scores (24). It is claimed that protein solubility is altered by the tissue salts, which are concentrated by freezing and remain in liquid solution at comparatively low temperatures (25), but the rate of deterioration at a given temperature differs widely among various species (26). This method is tedious and is subject to errors of at least 8% (27), while the results are further affected by the nutritional state and sexual maturity of the fish (28). There is also evidence that under certain conditions the taste panel rating may slowly fall, while no change is apparent in the protein solubility (29). Other properties of fish protein which have been studied in this connexion have been viscosity (30) and the combining ability with dyestuffs (31), but the usefulness of these properties has not yet been fully explored. It has been established that the difference between the amount of free sulphydryl groups and sulphydryl groups after addition of a protein denaturant ('masked sulphydryl') is useless as a measure of cold-storage change (32). A new method has been described (33a) which depends on differences in the fragility of the individual muscle cells when they are subjected to homogenisation. Results show less error than do protein solubility measurements (33b), and a good correlation with storage time. The method is rapid, and is probably the most promising technique so far described.

Studies of the effect of *post mortem* changes on fish subsequently frozen have shown that in fresh water fish (34) and cod (35) the size of ice crystals at a given freezing speed depends on the physiological state of the fish—if the fish is frozen before *rigor mortis* the ice crystals are much smaller than in fish frozen later. Nikkilä & Linko found (36) that Baltic herring frozen before *rigor mortis* deteriorated much more quickly in the cold store than those frozen after, but other workers have not found any great differences between fish frozen in different stages of *rigor* (26, 37).

### Salting

Comparatively little work has been reported on salting of fish over the last few years, although a selected bibliography of salt cod was published in 1957 (38).

Measurement of total volatile bases in pit cured fish (39a) and pickled fish (39b) gives a better index of spoilage than do trimethylamine values. Changes in protein (40) and fats (41) and prevention of bacterial and mould spoilage during salting have been investigated (42). The 'ropy' condition occurring in brines containing sugars is ascribed to levan production by certain bacteria (43) and the types of bacteria present on spoiling herring preserves have been investigated (42). Changes in the salt concentration of the medium can appreciably alter the biochemical activities of halophilic bacteria (44).

Methods for determination of salt concentration of fish muscle (45a) and acetic acid concentration of marinades (45b) have been described.

### Smoking

Advances in knowledge of the smoke-curing process were reported at two international conferences held in Gdansk, Poland; summaries of the first have already appeared (46) and proceedings of the second should be published shortly. Useful surveys of smoke curing have also been published (47).

Electrostatic smoking methods have been developed in many countries. These are of two types, in one of which smoke particles are charged and accelerated towards the target in the same electrical field (48) and a space charge system (49) in which charged particles deposit on fish under the influence of mutual repulsion forces. Electrostatically smoked fish are reported to differ in flavour and keeping quality from normally smoked fish (50, 51a) and the expected large increase in smoking rate has not been realised (50, 51b). The differences are explained by the discovery (51c, d, 52) that smoke vapours and smoke particles have different chemical compositions and that the normal smoking process is one of vapour absorption, deposition of particles contributing a maximum of 5% to the deposit of smoke on fish. There is, however, an equilibrium between the concentration of smoke constituents in the vapour phase and the concentration of smoke particles (51e), and optical density measurements therefore provide a useful, if indirect index of the rate of smoking (53a). Details of a recording smoke density meter (54) and of an ingenious integrating instrument, measuring smoke density  $\times$  time (55), have been published.

Continuous operating smoke producers are being developed. Some of these (56) are essentially mechanised devices for producing smoke by the traditional method of burning sawdust, but a novel type of generator, the 'fluidiser' (57), produces smoke by thermal degradation of wood, without actual combustion, in a controlled blast of hot air. Various types of 'friction generators' (58) appear to be gaining acceptance in the fish smoking trades in Europe and America. Each of these generators is claimed to give acceptably flavoured smoke products, although flavours are distinguishable from those of traditionally smoked fish (59).

Smoke 'dips' have been developed in at least three countries (60a). Although it is claimed that traditional smoking is physically related to a dipping process (61), that the dip is free from carcinogenic substances and that production costs of smoking by dipping are low (60b), the legality of this process of flavouring does not appear to have been tested.

Investigations of the chemistry and of the properties of wood smoke are proceeding. Phenols are reported to be the most im-

portant bactericides (53*b*, 61–63) and antioxidants (51*d*), but insufficient information on the nature of the odorous and flavouring components of smoke is available.

### Drying

Over the past few years the vacuum freeze-drying process has received much attention. The use of expanded metal plates (64) and microwave energy (65) during removal of bound water have speeded up the process without any loss of flavour or nutritive value (65*a*). A successful process of freeze-drying without a vacuum (66) and commercial production (67) of minced fish dried in warm air have been discussed.

Storage tests on pre-cooked, vacuum freeze-dried nitrogen-packed cod fillets showed that at 0° and 18° there was no difference in quality and they were still acceptable after 18 months, whereas at 37° they were unacceptable after 1 month. Similar results were obtained with raw fillets (68).

Recovery of moisture on reconstitution of vacuum freeze-dried fish is 100%, whereas recovery by fish dried in warm air is much less (69). Other factors affecting the recovery of moisture by dried fish include fat content and treatment prior to drying with antioxidants and sodium citrate or phosphate (70).

The translocation of potassium ions during the drying of muscle cells is thought to be an important factor concerned with toughness due to denaturation of the protein (71). Some fundamental work on the 'browning' of dried fish has been reported (68*a*, 72), and its prevention is possible by reduction of the moisture content to less than 1%, elimination of carbohydrates or treatment with sulphite (73).

### Fish canning

In the period under review (1955–60) steady rather than spectacular progress has been maintained.

The possible uses of tetracycline antibiotics in extending the storage life and improving the quality of fish for canning have been studied (74) with moderate success. Virtually none of the antibiotic survives heat processing (75). Contributions have been made to the general bacteriology of canned fish (76) and the cause of mushiness in South African pilchards explained (77).

Maillard-type reactions have been shown to be important in the browning of crab (78) and white fish (79). The nature of the off-colour in pre-cooked tuna has been related to changes in the muscle pigments (80) and a method has been suggested for detecting, before cooking, this tendency to discolour (81). Sulphide staining in tuna cans is due to the formation of iron sulphide, the critical factor being the presence of ferrous ions in the can during processing (82).

Rancidity and other problems connected with the canning of frozen salmon have received considerable attention from Tanikawa and his colleagues (83). The suppression of curd (84) and the development of a spectrophotometric method for predicting the colour of canned salmon from that of the raw fish (85) have been investigated.

A 'low-temperature' boiling of crabs, designed to lessen the incidence of bluing of the flesh during subsequent processing, has been introduced in Japan (86) and has led to problems which have been studied along with others relating to crab flesh (87).

The best conditions for the chill and cold-storage of fatty fish prior to canning have been investigated (88). The more widespread use of cold-storage should go far to alleviate supply difficulties arising from seasonal variations in catches.

Various methods have been described for pre-cooking Moroccan sardines (89), similar studies having been done on Portuguese sardines (90) and South African pilchards (91). Certain additives have been used for reducing the aqueous liquor in canned herring (92).

The suppression of struvite formation has received much attention from Japanese workers, especially with regard to crab and salmon (93). Sodium hexametaphosphate was partly successful but could not be used in the necessary concentration due to undesirable side effects. Similar results were observed with cray-fish (94).

Methods for measuring the freshness of fish before canning by examination of the canned material are still sought (95), the use of volatile reducing substances showing some promise (96). The condition of sardines can be assessed by following the breakdown of the belly-wall (97).

### **Fish meal**

This subject was last reviewed in 1955 and the present account is necessarily restricted to a few aspects of the industry in which applied chemistry is involved.

Chemical preservation of the raw material is generally subject to less stringent regulations than those which apply to products intended for human food, both sodium nitrite and formaldehyde being fairly widely used, even if sometimes without formal official approval. A report on British experiments (98) reviews many developments elsewhere; in addition Russian tests with nitrite (99) and East German tests with chlorinated water (100) may be noted.

Preservatives also permit control of autolysis in the manufacture of fish 'ensilages', where nitrite may be suitable if the product is later dried and much of the nitrite incidentally destroyed (101). Liquid ensilages usually rely on a low pH, sometimes assisted by

organic agents, e.g., molasses. The proteolytic enzymes may be those of the fish itself, or specially added. Denmark has always led in this field (102) but there is considerable recent interest in East Germany (103) and elsewhere (104).

Oxidation of oil in bulk stocks of freshly-prepared fish meal may lead to overheating and spontaneous combustion (105), and is a more serious problem with species of fish in which the oil is particularly unsaturated, e.g., the American menhaden and the South African sardine. Not surprisingly, therefore, the U.S.A. and South Africa have been in the forefront of research and industrial development aimed at preventing undue temperature rises in stocks of meal. The Americans have pioneered the use of anti-oxidants, which were introduced into the menhaden industry in 1955/56 (106). After DPPD (diphenyl-*p*-phenylenediamine) had been dropped as being too toxic (107), BHT (2,6-di-*t*-butyl-4-methylphenol) came into general use and eliminated the need for a lengthy 'curing' process (108). Various antioxidants have been tested (109) and 'Santoquin' (2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline) seems to be the most effective (109-110). The South Africans have concentrated rather on an adequate curing process and are not convinced that oil oxidation is the only, or even the main, source of heat (111). It has elsewhere been claimed (112) that an accelerated, but controlled, curing process is advantageous.

More-or-less tasteless and odourless fish meal (fish flour) is often advocated for supplementing protein-deficient human diets (113), surprisingly even within the U.S.A. and Canada (114). Its preparation always involves solvent extraction, usually with ethanol (115), although other solvents are sometimes used, either alone or in combination with ethanol, e.g., petroleum, isopropanol, ethyl acetate and acetone, or in combined azeotropic drying and oil extraction, e.g., ethylene dichloride. Various pilot schemes, sponsored by international or national government agencies (116), have so far failed to lead to full-scale commercial developments.

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## GENERAL MICROBIOLOGICAL PROCESSES

By MEMBERS OF THE MICROBIOLOGY GROUP  
(Convenor: T. G. TOMLINSON, M.Sc., B.Sc. Tech.)

### BREWING, MALTING AND ALLIED PROCESSES (J. R. A. Pollock, Ph.D., D.I.C.)

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#### Barley and malting

THE estimation of nitrogen-content in barley, perennially urgent at harvest time, is accelerated by directly distilling off ammonia from mixtures of the barley grist and aqueous sodium hydroxide (1) or by extracting with the latter solvent and estimating the extracted protein with sulphosalicylic acid (2). Loosening the husks with hot sodium hypochlorite offers a useful new way of estimating husk content (3).

Uniform and prompt germination being essential in making good malt, the phenomena of dormancy and water-sensitivity are of practical importance (4). Light may affect germination: partially dormant barley germinates best in the dark (1). The gradual elimination of dormancy during storage may reflect accumulation of acidic compounds able to stimulate germination in dormant barley (5). These substances are not gibberellins and they do not affect water-sensitivity, which, however, is found to be induced by coumarin (6) and reduced by treatment with calcium chloride or ammonium bifluoride (7). The hypothesis, advanced to explain the properties of water-sensitive barley (8), that the outer layers of the grain, and particularly the pericarp, interfere with the access of oxygen to the embryo has been supported by direct evidence (9). In German barleys the incidence of water-sensitivity and of full dormancy were parallel (10), but in a wide range of Australian barleys water-sensitivity was not observed (11). However, the rates of germination of the latter were used to establish a 'germination index' in which varieties useful for malting have medium values (11). A preliminary survey of the usefulness of this index in breeding new varieties was made (12).

Widespread interest continues to be shown in devising new ways of malting barley, the aim being to reduce the time taken and the losses incurred in converting barley into malt. In one such method,

in which barley is steeped for a short time, germinated for 3 days, again steeped and left in air for a further 3 days (13), the desired effects are obtained through inhibition of growth during and after the second steeping while the high eventual moisture content of the endosperm promotes rapid modification. In other methods, gibberellic acid plays a central part (14). The substance, applied to barley during or soon after steeping, substantially accelerates malting, treatments at the rate of 0.25–1.0 p.p.m. of the grain securing the most useful results. Claims for useful effects from still lower concentrations (e.g., 0.05 p.p.m.) must be scrutinised with care, for there may be an unbalance in the processes of modification whereby the rate of proteolysis is accelerated but carbohydrate modification unaffected. Although there is always a tendency for proteolysis to be especially rapid when gibberellic acid is used, this can be controlled by the simultaneous use of potassium bromate (15). 2,4-Dichlorophenoxyacetic acid (2,4-D) usefully restricts growth and, when used with gibberellin, yields malts of good analysis (16), although derived beers have unacceptable flavours and there is a difference of opinion as to whether diastatic activity is increased or decreased by 2,4-D (16, 17). The real function of gibberellic acid applied in malting is not yet fully understood. The compound itself occurs in barley partly free and partly in a bound form from which it is released as germination occurs (18). In sterile endosperms from which the embryos have been removed gibberellic acid induces the formation of amylase (19) and it seems likely that it is in fact the substance, having the same powers, which has been shown to be secreted by the germinating embryo (20).

Ways of predicting the ease with which barley can be malted continue to attract attention. A 'steeping index', based on the rate at which the grain absorbs water, gave initially very favourable results (21). Both the sclerometer and the Brabender hardness tester give useful indications of friability in malt (22, 23), sclerometer values being related to fine-coarse grind extract differences and to the Hartong index but not so well to the Kolbach index (23).

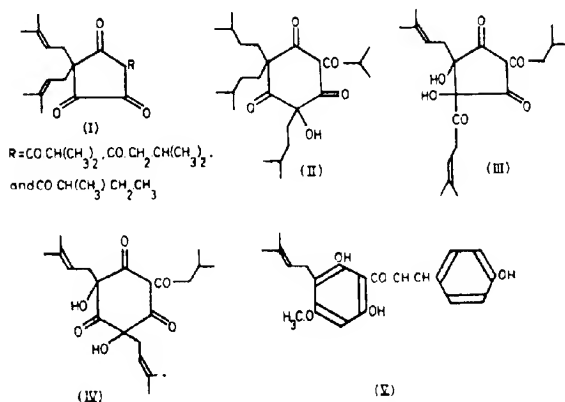
The anthocyanogens of barley—closely involved in haze formation in bottled beers—scarcely vary in amount during ordinary malting, although green malt contains enzymes capable of destroying these polyphenols oxidatively. In grain from which the husks and pericarp have been removed, the anthocyanogens are leached out during steeping and, as oxygen can penetrate in this case, the residual anthocyanogens within the grain are later destroyed enzymically (9).

### Hops

Although excellent methods are available for estimating the bitter acids of hops both jointly (24, 25) and severally (26) and

information is accumulating about the rôle of hop oil in beer flavour, the main mode of appraisal of hops is still evaluation by eye (27). Perhaps this is because certainty is lacking with regard to the nature of the compounds present in beer which are derived from hops and because of the fact that although the  $\alpha$ -acids account for 85% of the bittering power of fresh hops, they are destroyed much more rapidly than bittering power during storage (28). It is suggested that empirically useful estimates of the bittering power of hops can be made by estimating the  $\alpha$ -acid content at picking, adjusting for cohumulone content (which yields more bitterness than humulone or adhumulone) and reducing the value by 7-10% for each year of cold storage (28). However, the possibility of controlling hop picking by analysis still seems remote because of the gross variations observed between the  $\alpha$ -acid contents of cones from individual plants (29).

The hulupones, a new group of hop bitter substances, are represented by structure I (30). The formally obvious relationship with lupulone is supported by the preparation of tetrahydrocoulupone from hexahydrocoulupulone by aerial oxidation and thermal decomposition of the resultant peroxide (31). The peroxide yields, on hydrogenation, a compound formulated as hexahydrocoulupulinone (II) which can also be transformed into tetrahydrocoulupone (32). Doubtless reactions like these occur during the ordinary storage of hops. Humulinone, the product obtained by peroxide oxidation of humulone, has been shown to be III rather than IV (27). The structure of xanthohumol has been revised to V (33).



The inefficient utilisation of hops in ordinary brewing, which is not due to insolubility of the isohumulones (34) and which can be



improved by use of ultrasonic irradiation (35), continues to lead to new ways of making suitable hop extracts. In particular a method in which ion-exchange resins are used to adsorb, separate and isomerise the  $\alpha$ -acids is promising (36).

It is generally accepted that hop oil constituents have an important effect on beer flavour and threshold flavour limits for several oil fractions have been determined (37), but actual constituents have only recently been shown to occur in beer. These are caryophyllene, humulene, isocaryophyllene, farnesene, myrcene and 2-undecanone (38). Ocimene has been identified chromatographically in hop oil (39).

#### *Brewing processes*

An integrated continuous pilot-scale brewery providing for mashing, hop boiling and fermentation has been described (40); it incorporates the rotary mash-tun discussed in an earlier report (41). The resulting stream of sweet wort is boiled and passed in countercurrent fashion through a moving bed of hops formed on an endless perforate belt, after which the hopped wort passes to receiving vessels and thence is fed continuously to two enclosed stirred fermentors which can be used singly or in series. The resulting mixture of beer and yeast next flows through a cooled, divided vessel in which the yeast sediments out and from which the beer flows to be collected. In newly described continuous mashing plant, conversion of mash is made in a series of compartments held at different temperatures, the detailed conditions applied at this time determining the composition of the eventual wort (42). Following this, separation is achieved on vibrating screens, in settling tanks and by centrifugation.

Because the rate of fermentation depends upon the concentration of yeast in the fermenting liquid, control of this factor is important in continuous operation. Three main methods are now described for achieving yeast concentrations above the equilibrium level: (1) the effluent yeast may be collected and part of it returned to the fermentor (43); (2) growth may be brought about in an aerobic phase to give a controlled amount of yeast which then passes forward with the wort to anaerobic fermentors (44); (3) use may be made of the flocculative characteristics of yeast to cause it to settle back into the fermentor when the mixture of beer and yeast pass through an unagitated zone before they escape (45). Infection with unwanted micro-organisms is potentially more dangerous in continuous than in batch fermentations; in this respect single-vessel systems are shown to be safer than those where several vessels are used in series (46).

#### **Yeast**

Storing yeasts in the freeze-dry condition enables cultures to be

maintained for long periods (47), although changes take place in dried yeast which lead to the rapid excretion of enzymes when the yeast is again wetted, and to diminution of fermentative activity (48). Storage at  $-20.5^{\circ}$  is said to permit long keeping of bulk compressed yeast without deterioration (49). In a study of the bacterial contamination of pitching yeasts observations were made which suggested that one of the yeasts used produced an antibiotic against beer bacteria (50).

Respiratory-deficient yeasts are potentially interesting in brewing because of their relatively economical production of alcohol. Mutation to deficient respiration occurs naturally faster at either relatively high or low temperatures than at medium temperatures (51, 52) and is induced by ultra-violet irradiation (53) or by allyl-glycine, the last effect being suppressed in the presence of cysteine (54). Less completely deficient respiration is shown by *Saccharomyces carlsbergensis* growing aerobically in presence of glucose, ethanol or acetate, although ability to respire these substrates is acquired inductively during cultivation on them. The block is located in succinic dehydrogenase (55). A related degenerative and reversible loss of fermentative ability occurs in stationary yeast cultures in the presence of glucose (56). Many of the enzymic activities of yeasts are inducible or repressible by suitable techniques and it has been predicted that such methods will be adapted to serve applied microbiology extensively (57). In brewing, the mechanisms by which maltose and maltotriose are taken into the yeast cell are enzymic, the relevant permeases being formed inductively in response to the substrates. The activity of the relevant permeases is probably a limiting factor in the rate of utilisation of these sugars (58). In a fuller understanding of these and related matters more knowledge is needed of the ways in which enzyme synthesis is induced or repressed (59) and of the general mode of protein synthesis in yeast.

A newly recognised group of peptide nucleotide complexes, in which a phosphoanhydride link is formed with the carboxyl group of the peptide, are considered to function intermediately in protein synthesis (60a). Among the numerous substances of this type shown to be present in yeast (60a), arginylalanylargininylalanyl-5'-uridyate (60b) and alanyl-(3'-5'-adenylyl)-5'-uridyate have been identified (61), while in further members of the group other nucleotides (61) or dinucleotides (60b) are united with other peptides (62). Adenine and uracil absorbed into yeast pass via such compounds through a series of nucleotides of gradually increasing complexity (63). The peptidyl nucleotides in growing yeast increase markedly both when logarithmic growth is initiated and when the rate of growth decreases (60a). Variations of these compounds in synchronously dividing yeast cell populations have not been reported, but during budding the deoxyribonucleic acid is

rapidly doubled and thereafter remains constant until the next period of budding. The ribonucleic acid content, however, increases steadily during the growth of buds and ceases at cleavage, a similar cycle being reproduced at the next budding (64).

### Beer

Recognition of the rôle of certain anthocyanogens in beer hazes has led to further study of the properties of beers filtered through nylon powder to remove these compounds (64a), and it is recognised that such treatment may usefully shorten the lagging time (65). Numerous other polymeric amides will also adsorb anthocyanogens from beer (66). An alcohol-soluble protein of beer has been recognised as the main protein component of haze, while another protein fraction from beer induces stability against development of haze (67).

Apart from its accelerating influence on the formation of hazes in beer, oxygen may mar beer flavour. Certain beers contain natural antioxidants which stabilise them to some extent in this respect (68), but for others stabilisation with added ascorbic acid (69), adenine (70) or 3,4,5-trihydroxybutyrophenone (71) have been considered.

New techniques are allowing gradual progress to be made in defining beer flavour (72). Gas chromatography readily reveals in beer the presence of acetaldehyde, acetone, ethyl acetate, ethyl formate, methyl acetate, methanol, 2-propanol, 2-methyl-1-propanol (a), 2-methyl-1-butanol (b), 3-methyl-1-butanol (c), 1-pentanol and phenylethyl alcohol (d) (28, 73a-c). Of these, (a), (b), (c) and (d) are produced during fermentation from the homologous amino-acids (73c), while (b) is also formed from threonine and 2-aminobutyric acid (74) and 2-propanol is believed to be derived from 2-oxobutyric ( $\alpha$ -ketobutyric) acid (75).

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### NON-MEDICAL USES OF ANTIBIOTICS (J. Vernon, B.Sc., Ph.D.)

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ALTHOUGH non-medical uses of antibiotics have not previously been covered in these Reports, it is proposed to review developments during the past 12-18 months only. Details of the discovery of non-medical uses and previous progress can be found in many excellent reviews (1-6).

The three antibiotics, chlortetracycline, oxytetracycline and penicillin, have continued to be the most used in animal feeding. Bacitracin and streptomycin are less frequently used, but more often in combination with one of the other three. Other growth-promoting antibiotics include erythromycin, gramicidin, neomycin, oleandomycin, spiramycin and tyrothricin.

### Nutritional uses

#### (a) Chickens

The effects on rate of liveweight gain and efficiency of feed conversion of the three most-used antibiotics have been studied in countries where previously only a very limited amount of investigational work had been conducted (7-9). In addition, there have been reports of work with oleandomycin confirming earlier findings of its efficacy at very low levels, 1-2 g./ton of feed (10, 11).

It has been suggested that antibiotics are no longer affording responses in terms of improved rate of liveweight gain comparable with those recorded when they were first introduced. Evidence has appeared which suggests that this is not the case (12-14). Heth & Bird (14) have summarised the results of 61 trials with penicillin over a period of 9 years and showed that responses did not diminish over this period. Results with chlortetracycline and oxytetracycline were, if anything, slightly better than those given by penicillin, in that only 6 out of 49 trials failed to give a response over a similar period.

Antibiotics have been implicated in the haemorrhagic condition in poultry which is responsible for the down-grading of a large number of table birds in the U.S.A. Dempsey & Sandford (15) have recently presented data suggesting that various antibiotic supplements can cause significant increases in haemorrhage and that there is an interaction between antibiotic and diet. Crystalline forms of antibiotics were shown to cause significantly less haemorrhages than crude feed-grade preparations, but the effects were not consistent and obviously further work is necessary.

Conflicting results are available concerning the liveweight gain-promoting effect of inactivated penicillin preparations. The latter have been further investigated by Coates & Harrison (16) under conditions where a response to penicillin is regularly obtained. Penicillin improved rate of liveweight gain but *d*-penicillamine had no effect. Stephenson & Robertson (17), however, who had previously reported (18) that penicillamine was effective in promoting growth when injected but not when given orally, have shown that oral penicillamine is destroyed or bound in the proventriculus, so that it might not be available to the bird further down the gut. Excretion of parenterally-administered material into the lower part of the intestine could occur, however, and this may account for the difference in results.

The supplementation with enzyme preparations of broiler diets containing a high percentage of barley, and the use of water-treated barley, have attracted a considerable amount of attention. It has recently been suggested (19), however, that the superiority of water-treated barley over barley plus enzyme supplements was due

to the presence of an effective antibiotic in the water-treated material.

(b) *Turkeys*

Waibel *et al.* (20) suggest that the response to antibiotics in turkey diets may depend upon the period for which antibiotics have been in use in a particular environment. Penicillin, which had been used continuously over a number of years in their facilities, gave smaller responses than other antibiotics which had not been in continuous use.

(c) *Layers*

The continuous feeding of antibiotics to laying hens has continued to give variable results as judged by effects on egg production and feed conversion efficiency. The magnitude of the response generally appears to vary according to environmental conditions (21) and level of production of control birds receiving no antibiotic (22, 23). Rosen *et al.* (24) reported earlier this year the results of an experiment with individually recorded laying hens, which formed part of a multi-centre investigation in which a significant relationship was observed between the level of egg production of the control birds and the response to oxytetracycline at 25 g./ton of feed on a flock basis. With the individually recorded birds, however, it was possible to show that, within a low-producing flock, the birds that responded were not the lowest producers, but those of medium-range production.

Two interesting reports have also been issued (25) of experiments in which the effects of an antibiotic in the diet were compared with those of an equivalent level of antibiotic given in the drinking water. It would appear that the two methods are equally effective as measured by improvement in egg production.

(d) *Pigs*

As with chickens, there has been a continuation of studies demonstrating the effects of various antibiotics on rate of liveweight gain and efficiency of feed conversion. Work with newer antibiotics such as spiramycin (26) has shown these to be effective for pigs. It has also been confirmed (27) that antibiotics are without effect on carcass quality. Furthermore, it has been shown (28) that antibiotics have no significant effect on sexual functioning when fed continuously during rearing stages.

Copper sulphate at a level of 0.1% of the diet can improve the rate of liveweight gain of growing/fattening pigs to a similar extent as antibiotics (29a, b). Conflicting data are available, however, concerning the interaction between these supplements (29a, c). Additive effects have been reported (29c), but as yet, the circumstances under which these occur have not been defined. Environ-

ment has been shown to affect the response to both supplements when they are fed alone (30).

(e) *Lambs*

The use of antibiotics in lamb feeds has been extended to include oleandomycin (31) which improves the rate of liveweight gain. Antibiotic injections, or implants, are without effect (32).

(f) *Calves*

The liveweight gain-promoting properties of antibiotics for calves have been further confirmed (33).

(g) *Dairy cows*

While the feeding of antibiotics to pigs, poultry and calves has been widely accepted, their feeding to lactating ruminants has not. Early reports on the feeding of the broad-spectrum antibiotics to dairy cows were somewhat contradictory (34). Furthermore, it is known that the presence of antibiotics in milk will render it useless for cheese making and therefore there have been doubts about the practicability of feeding antibiotics to lactating animals in case of carry-over into the milk. During the period under review, further conflicting data have appeared showing no response (35) and responses (36) in terms of increased milk yield from the continuous feeding of antibiotic. These last references are to large-scale field investigations that have been conducted with chlortetracycline at 0.1 mg./lb. liveweight/day (36a) and oxytetracycline at 75 mg./head/day (36b) and in which satisfactory economic returns have been obtained from antibiotic supplementation. The results of these investigations justifies further extension of this work.

(h) *Beef cattle*

Progress in this particular field has been confined to demonstrating that the effect of antibiotics in promoting liveweight gain is maintained in the presence of other additives such as hormones and tranquillisers (37).

### **Mode of action of antibiotics in improvement of liveweight gain**

Various theories have been put forward to account for the mode of action of antibiotics in improving the rate of liveweight gain of farm animals. These have included hypotheses on the effects upon the gut flora and also on the absorption of certain essential nutrients. In connexion with the latter effect, further reports have appeared showing that oral antibiotic reduces the requirement of the turkey poults for potassium (38), and that calcium and magnesium absorption are improved in the rat (39).

It was observed, during a clinical study of the effect of various dietary fats on serum lipids of a group of patients with atherosclerosis, that the oral administration of neomycin to a patient was associated with a significant fall in serum cholesterol concentration (40a). In a subsequent study with ten patients, a significant decrease in serum cholesterol was recorded in all cases with a daily intake of neomycin of 1.5–2.0 g./head. Later it was shown that intra-muscular administration of neomycin had no effect, although oral administration again reduced levels in all cases (40b). No significant changes occurred with oral bacitracin, novobiocin or polymixin-B sulphate. On the other hand (41), prolonged administration of neomycin to cholesterol-fed rabbits resulted in an elevation of serum lipids and more severe aortic atherosclerosis and visceral lipoidosis than in untreated cholesterol-fed controls. As intramuscular injections of neomycin did not give similar results, it is suggested that the effect is due to increased absorption of cholesterol when the antibiotic is given in the diet. Oral neomycin with non-cholesterol-containing diets did not affect serum cholesterol levels in this species. This species difference sounds a warning note that, species-wise, generalisations should be avoided for antibiotic effects.

Work with germ-free animals has been extended to include studies with penicillin in the diet of chicken whose gut has been intentionally populated with certain bacteria (42). The results lend support to the theory that *Clostridium welchii* is one factor in the 'growth-depressing infection' that is counteracted by dietary penicillin. Of the organisms that were introduced into the gut of germ-free animals, only *Clostridium welchii* type A caused a depression of liveweight gain compared with that of controls. Penicillin counteracted this effect.

It has also been suggested (43) that antibiotics have their effect on the physiology of bacteria rather than on the numbers or types of intestinal forms and that, as a consequence of antibiotic feeding, the organisms are rendered more susceptible to natural body defence mechanisms, i.e. phagocytosis. These studies have been extended to the dairy calf (44). Comparisons have been made of the effects of age, colostrum and chlortetracycline feeding on the susceptibility of intestinal coliform bacteria to phagocytosis. Bacteria isolated from the faeces of chlortetracycline-fed calves were more susceptible to phagocytosis than bacteria from unsupplemented animals. The phagocytic index for antibiotic-fed calves increased faster and reached a maximum at an earlier age than with calves fed no antibiotic.

Additional evidence to support the theory that antibiotics have their effect within the gastro-intestinal tract has been presented by Jowsey *et al.* (45). Similar results were obtained in turkeys fed low levels of penicillin or given large intraperitoneal injections. The

large injections gave the same level of penicillin activity in the gut as did the low level in the feed.

### Antibiotic potentiation

While the potentiation of blood levels of orally-administered antibiotics is aimed primarily at increasing their effectiveness for the treatment of disease, the levels of antibiotics studied have been lower than those normally used therapeutically. This particular field of antibiotic research has become particularly active during the past 12-18 months in agricultural spheres. Two methods have commonly been used for the enhancement of blood levels of antibiotic, firstly the use of organic carboxylic acids, particularly terephthalic acid (46), and secondly, the use of diets containing a very low calcium content. These two methods of potentiation have been shown to be complementary. Calcium appears to inhibit the absorption of antibiotics through the gut wall into the blood stream and terephthalic acid to increase the renal threshold, thereby reducing antibiotic urinary excretion (47). Parenterally administered salts of terephthalic acid have a similar potentiating effect to the orally administered acid (48).

Very high levels of chlortetracycline, 600 and 800 g./ton, impart a yellow tinge to egg shells which was intensified by addition of terephthalic acid (49). The discoloration was not observed in the shell membrane and oxytetracycline supplements did not produce similar effects.

### Antibiotic-resistant organisms

It is well known that the feeding of an antibiotic is attended by changes in the sensitivity to that antibiotic of micro-organisms within the gut of the animal. Work by Garside *et al.* (50) with poultry indicates that resistant strains of *Salmonella typhimurium* had arisen from sensitive strains which had been introduced by oral inoculation. While no change in virulence or pathogenicity of the organism was associated with the changing resistance-sensitivity pattern, and while the inclusion of the antibiotic in the diet afforded some measure of protection against disease, as reflected by reduced mortality of infected birds, there was evidence of a large number of carriers occurring in the antibiotic-fed chicks. The significance of these findings is discussed.

The proportion of antibiotic-resistant strains of *Staphylococcus aureus* isolated from the nose and skin of pigs, chickens and their attendants, has been shown to be higher as a result of antibiotic feeding (51). The widespread use of antibiotics in Great Britain, however, does not appear to have affected the sensitivity of *Salmonellae* in the general pig population (52).

There continues to be some apprehension regarding the possible risk of human infection from the emergence of resistant strains of



potentially pathogenic organisms in animals. This has been discussed in some detail with respect to *Salmonellae*, *E. coli* and *Streptococci* in a recent publication (53) which clearly indicates the value of and the need for more long-term studies in this connexion.

### Food preservation

Further publications have confirmed that certain antibiotics under specified conditions can reduce significantly losses of poultry meat from bacterial spoilage (54). It has also been shown that terephthalic acid and/or low-calcium diets in conjunction with antibiotic feeding can even further extend shelf life in poultry (55). Serum- and tissue-levels of antibiotic at slaughter were higher and shelf life was greater when the treatments had been given for only one day rather than eleven.

In general, the improvements observed in the keeping quality of poultry have been greater under laboratory than commercial conditions, which may be associated with the development of resistant strains of bacteria in the latter (56).

### Plant disease

Work with antibiotics in the field of plant disease has continued to make steady progress.

Streptomycin is known to have no antifungal activity *in vitro*, but small quantities absorbed by roots of tomato and potato plants have shown marked antifungal effects in the foliage (57). The *in vivo* activity can be increased by mixing the antibiotic with water-insoluble copper fungicides (58). A streptomycin-copper chelate (59) has shown even greater antifungal protection in greenhouse tests against *Phytophthora infestans*, the activity of the preparation being approximately six times that of streptomycin sulphate and approximately three times that of a mixture containing equivalent amounts of streptomycin and copper.

The development of antibiotic-resistant strains of phytopathogenic bacteria has been repeatedly demonstrated in the laboratory but has not yet been shown to create problems in practice. The recent report (60) of the emergence of antibiotic-resistant strains of *Pseudomonas tabaci* during field investigations in which several antibiotics were compared with copper fungicides for the control of wildfire and angular leaf spot of tobacco is therefore of some interest. It is obvious that, as with animals, a closer study is necessary of the development of antibiotic resistance and its practical significance.

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### MICROBIOLOGY OF WATER AND SEWAGE (E. Windle Taylor, M.A., M.D., D.P.H., and N. P. Burman, B.Sc., Ph.D.)

#### Metropolitan Water Board

#### Viruses

AN extensive survey by the Public Health Laboratory Service (1) for the presence of polio virus in sewage covering 96 communities resulted in only three successful isolations. This low incidence contrasts markedly with results obtained by Kelly & Sanderson (2), who found that 90% of the sewage samples examined contained enteroviruses. Treatment on trickling filters did not reduce the

frequency of isolation, and chlorination often, but not always, reduced the frequency and the concentration of particles determined by a plaque technique. Additional methods of sterilisation are suggested as being preferable to increased chlorination of effluents in order to achieve viral sterility. Ryzhov & Shtannikov (3) in Russia have shown that effective disinfection of water infected with poliomyelitis virus can be achieved in 30 min. with 0.5–2.1 mg. per litre of residual chlorine. The effect of water treatment processes on virus removal has been studied by Pascoe (4), who used bacteriophage. Coagulation with 60 mg. of ferric chloride per litre gave optimum removal at pH 6.5 when 99% of phage was removed. Sand filtration also removed the phage, probably by electrostatic adsorption.

In an extensive survey of the literature, Clarke & Shih Lu Chang (5) assert that infectious hepatitis is still the only virus disease conclusively established as having been carried by water, although a few poliomyelitis outbreaks are suspect.

### Disinfection

The viability of *E. coli* after exposure to chlorine will depend on the culture medium used for subsequent growth. Milbauer & Grossowicz (6a) achieved reactivation on rich nutrient agar, whereas growth failed on a minimal agar. Furthermore, they showed (6b) that cultures of *E. coli* grown on rich nutrient agar were much more resistant to the action of chlorine and were more easily reactivated than those grown on minimal agar.

The sporicidal activity of free available chlorine towards *Bacillus globigii* and *B. anthracis* has been studied by Brazis *et al.* (7). Increase in pH, decrease in exposure time and decrease in temperature all increased the amount of chlorine required to achieve a 99.99% kill. The mechanism of the bactericidal action of chlorine has been attributed by Trakhtman (8) to inhibition of the earlier stages of carbohydrate metabolism as a result of experiments showing that chlorine at 40 mg. per litre inhibits the action of glucose dehydrogenase by 90.8% and peroxidase by only 30%.

The discovery of nematodes in a city water supply derived from the Ohio river has led Shih Lu Chang *et al.* (9) to report that pathogenic bacteria and viruses ingested by these nematodes will be protected from the destructive action of free residual chlorine.

Free bromine and monobromamine have been studied as bactericidal agents by Johansson (10) with results similar to those for monochloramine, whereas iodine has been found to have some advantages as a sterilising agent for swimming pools (11). The desired residual of 0.2 mg. per litre could be maintained with a smaller dose of iodine than of chlorine and is unaffected by ammonia derived from the bathers.

### Survival and antagonism

The survival of *Salmonella* and *Shigella* in water and other substrates may be ascribed to limitation of nutrients or the presence of antagonistic factors. The conclusions of different workers seem to depend on the particular waters or other substrates studied. McKinney *et al.* (12) have shown that *Salm. typhi* dies off very rapidly in high-rate sludge digesters and this has been attributed to competition for food, the essential factor limiting growth of *Salm. typhi* being tryptophan (13). Antagonistic factors appeared to make no significant contribution. Dyadichev (14), studying the survival and multiplication of *Salmonella* and *Shigella* in tap water, also attributed inhibition to a lack of sufficient concentration of organic substances suitable for bacterial nutrition.

Meyer (15), on the other hand, studying the survival of *Salmonella* in deep well water demonstrated the presence of a natural thermostable bactericidal agent, which could be absorbed on and eluted from ferric hydroxide. In sea-water destruction of *Salm. typhi* and *E. coli* (16a) and of *Shigella* (16b) was fairly rapid (1-5 days) and was attributed to thermolabile bactericidal factors other than bacteriophage. The bactericidal activity of sea-water has been attributed to antibiotic substances produced by planktonic marine algae. Allen & Dawson (17) extracted at least four different bactericidal substances from benthic tropical marine algae having a wide activity against Gram-positive but no activity against Gram-negative bacteria.

### Bathing places

The results of a large-scale comprehensive study of 40 bathing beaches by the Public Health Laboratory Service has been published during the year (18). Salmonellae of 33 different species were found in small numbers in 40% of the samples of sea-water containing over 10,000 coliforms per 100 ml. but it was concluded that bathing in sewage-polluted sea-water carries only a negligible risk to health and that such a risk is probably associated with chance contact with intact aggregates of faecal material. In a memorandum (19) based on this report, it is stated that disintegration of faecal masses might be desirable on health grounds as well as aesthetically where gross visible contamination of beaches is occurring, but no definite recommendation is made to this effect.

Following the suggestion that bacteria tend to become concentrated on the surface of swimming pools, Dick *et al.* (20) made an investigation of surface films collected by adsorption on alginate gauze lowered to the surface of the water for a few seconds. The gauze was then dissolved in 10% sodium hexametaphosphate and the solution plated on a suitable agar medium. There was some degree of surface concentration but not to any considerable extent.

The predominant organisms, however, were from the upper respiratory tract, often in clumps, and were resistant to chlorine.

### **Salmonella**

Two unusual sources of *Salmonella* have recently been recorded; one a direct infection with *Salm. newport* from pet tortoises in Holland (21), and the other, pollution of the Dakar City water supply from a tank reservoir exposed to heavy contamination from lizards (22).

There have been no outstanding advances in techniques for isolation of *Salmonella* but there have been the usual number of modifications of techniques and media. Robinson (23) has modified Moore's sewage swab technique by using alginate pads and subsequently dissolving the alginate in 10% sodium hexametaphosphate. Smith (24a) was unable to demonstrate any increase in selectivity by the addition of lactose to selenite broth, but mannitol could be an advantage depending on the associated organisms, with a further improvement on adding gentian violet. He also considered that the selective action of selenite broth may be due to the presence of seleno-polythionates which act as growth-inhibitory analogues of highly preferred sulphur sources and related this to the importance of the peptone used (24b). Bloom *et al.* (25) found improved results with a Brilliant green selenite broth, and Rappaport & Konforti (26) used a Malachite green-magnesium chloride enrichment medium. The magnesium was necessary to counteract the toxic effect of the dye on *Salmonella*. The superiority of one medium over another appears to be a matter of opinion, but all workers are agreed that a combination of several media will give better results than any one singly.

The number of rapid differential tests for *Salmonella* is now legion and every bacteriologist has his own favourite modification. Papadakis (27) has introduced yet another dulcitol-sucrose-salicin-iron-urea agar, a one-tube multiple medium with different ingredients in butt and slope. A further modification of a similar medium by Rappaport *et al.* (28) prevents deterioration by storage of the mixed ingredients dry and adding a self-sterilising urea-thiosulphate solution before use.

Gol'dfarb & Ostrovskaja (29) investigated methods for detecting *Salm. typhi* in water by the increase in phage titre. With a highly specific Vi-phage, 10-20 *Salm. typhi* per litre were detected within 20-22 hours' incubation. *Salm. typhi* could be isolated from artificially infected tap water up to 20 days but increase in phage titre could be detected up to 150 days.

### **The coliform group**

Levin *et al.* (30) have made further advances with the rapid radioactive tracer technique for detection of coliform organisms.

Sodium  $^{14}\text{C}$ -formate (0.01%) incorporated in Brilliant green lactose-bile broth has been substituted for radioactive lactose. The filter membrane is placed in a planchet with the medium, the whole contained inside a wide-mouthed, screw-capped jar and incubated for 3 h. at  $37^\circ$ . A planchet containing saturated baryta water is placed alongside for a further 1 h. to absorb the evolved  $^{14}\text{CO}_2$ . This simple procedure replaces the previous elaborate continuous-flow gas-trapping device.

There have been several comparisons of a variety of media for the presumptive coliform test (31), with particular reference to media containing Teepol or other surface-active agents as inhibitory substances or to chemically defined media based on glutamic acid compared with MacConkey broth and lactose broth. There was close agreement between all media for the total numbers of coliform organisms isolated in 48 hours. Non-inhibitory media such as lactose broth produced the highest numbers of false positives. Glucose-glutamic acid media produced high numbers of false positives with some samples but not with others, depending probably on the frequency of glucose-fermenting organisms. Burman & Oliver's lactose modification (31b) of glutamic acid recovered higher numbers of *E. coli* at the expense of other coliforms but growth was slow, especially of other coliforms. Gray's modification, known as formate lactose glutamate, containing 0.025% of sodium formate at pH 6.7, has largely overcome these drawbacks and further improvements are still under consideration (31d).

Hopton (32) showed that the onset of gas production by a coliform culture was determined by the concentration of undissociated formic acid, but that a higher concentration was required to elicit response at  $37^\circ$  than at  $30^\circ$ . Gas was not produced on unbuffered medium at  $37^\circ$  because pH and formate concentration became inhibitory before elaboration of hydrogenylase commenced. Formic hydrogenylase (FHL) is adaptive and readily inactivated and it is possible (33) to distinguish its activity in *E. coli* isolated from faeces and water, the amount being remarkably lower in the latter. FHL activity declined on storage of faecal *E. coli* in water, the reduction being progressive.

The interference of other organisms with the growth of *E. coli* in mixed cultures has been studied from time to time and various techniques have been suggested for limiting it. There was no significant interference from *Achromobacter*, *Micrococcus*, *Proteus* and *Pseudomonas* but other coliform organisms did cause some retardation or inhibition of *E. coli* at  $37^\circ$ , although this was much less marked at  $42^\circ$  (34). Burkhardt & Legler (35) found considerable interference from streptococci at  $45^\circ$  due mainly to reduction in pH. Dixon (36), working with pathogenic and non-pathogenic strains of *E. coli* showed that mixed cultures of two or more strains

growing in non-inhibitory media always tended to reach equality in numbers of all strains irrespective of the initial numbers present. The inclusion of other organisms, however, often resulted in their domination of the mixed culture when incubated at 37° but most other organisms were suppressed at 44°.

A combination of lactose fermentation and indole production at 44° has for some time been regarded as satisfactory presumptive evidence of the presence of *E. coli* in most parts of the world. Katugampola & Assim (37) have shown, however, that this is not true for Ceylon, as all coliform types isolated which gave indole at 37° also produced it at 44°, and these formed 8% of the total colonies fermenting lactose at 44°. To test the suitability of culture media for indole production at 44°, Windle Taylor (38) reports that *E. coli* cultures were selected which produced weak or negative indole results in 6 hours and positive results in 24 hours. The most suitable peptone of the five tested was Oxoid tryptone at a concentration of 2% without added tryptophan. The inhibition of indole production by fermentable carbohydrates has always prevented the introduction of a suitable medium to combine the two tests, but Velicangil & Demirhindi (39) have produced a medium which combines fermentation of mannitol with indole production. Worthen *et al.* (40) have used fermentation of glycosides to differentiate members of the Enterobacteriaceae, e.g., methyl- $\alpha$ -D-glucoside and arbutin to differentiate *E. coli* from *Klebsiella aerogenes*.

Thomas *et al.* (41), investigating coliform bacteria from farm water supplies, found that isolation at 30° was as selective for *Klebsiella* as 37° was for *E. coli*. Strains of *Citrobacter* and *Klebsiella* negative at 37° were the predominant organisms in protected wells of good sanitary quality whereas *E. coli* was the dominant organism in polluted samples, comprising 43% of the isolates at 30° and 76% of those at 37°. Gyllenberg *et al.* (42) investigated the possible significance of *Lactobacillus bifidus* as a suitable indicator of faecal contamination of water. They occur in faeces in numbers 10–100 times greater than coliform bacteria and are not known to grow in other natural environments. Survival rates were similar to those of coliform organisms in water but there was a relatively greater decrease under warm than under cold conditions. Selective methods utilising chemically defined media for isolation of these organisms are described (43).

#### Faecal streptococci

Two new procedures for detecting enterococci in water have been described. Guthof & Dammann (44) used a dextrose azide broth with 3% sodium chloride at pH 8.3 followed by subculture on a selenite plate. Morelis & Colobert (45) obtained luxuriant growth in 8–12 h. under semi-anaerobic conditions in an aesculin



azide broth containing glycine and iron ammonium citrate at pH 9.0. In order to increase the reliability of differential tests at high pH, Chesbro & Evans (46) recommended a tryptose-yeast-extract-glucose broth containing 0.05 M-sodium carbonate and 0.05% Tween 80, which permitted initiation of growth up to pH 10.5. Another useful simple differential test introduced by Spaander & Roest (47) is utilisation of citrate, detected by precipitation with lead acetate. All strains of *Streptococcus faecalis* gave positive results.

### Membrane filtration

Windle Taylor (48) and Burman (49) have introduced a number of improvements in membrane filtration techniques for coliform and *E. coli* counts including re-use of English membranes up to ten times by washing in running water; resuscitation of coliform counts on MacConkey broth at 30° for the first 4 h., thus avoiding the necessity to transfer from one medium to another; inclusion of 3% lactose in the resuscitation broth for *E. coli* counts; the substitution of 5% and 0.5% Teepol broth for MacConkey broth for the coliform and *B. coli* counts respectively; incubation for 18 h. at 35° to achieve coliform counts on membranes equivalent to 48-h. counts on multiple tubes; and incubation of membranes in small glass Petri dishes inside a larger container for adequate moisture control and so avoiding inhibitory action of tin containers. Noble & Reitman (50) demonstrated the inhibitory action of tin containers and McCarthy & Delaney (51) demonstrated the failure of the slow lactose fermenters which normally ferment lactose in liquid media only between 24 and 48 h., to produce typical colonies on Endo membranes. *Klebsiella* strains responded well to addition of sucrose and *Citrobacter* to addition of eosin to the medium.

Chibrikova *et al.* (52) have described a rapid membrane technique for detecting *Vibrio comma* in water by staining with acridine orange after 8-9 hours' incubation. Membranes have been used (53) for counting numbers of organisms in micro-quantities of suspensions of high numbers by prefixing in picric acid, filtering through an area restricted by greased circles and staining with acid fuchsin.

Schyma *et al.* (54) have introduced an entirely new micro-filter of aluminium alginate able to redissolve under physiological conditions which will retain particles down to 5-8  $\mu$  in diameter.

### Aquatic actinomycetes and fungi

A complete life-cycle of aquatic actinomycetes has been described (55), the odour varying with the particular stage in the cycle. Nutritional requirements have been studied and taste and odour compounds have been separated for further study (56). The International Committee on Bacteriological Nomenclature are

sorting out much of the taxonomical confusion in the Actinomycetes and to this end Kuester (57) has outlined the criteria to be investigated for selection of those most suitable for characterising the taxa, and Lessel (58) has listed all the genetic names of the Actinomycetales to facilitate selection of the correct names.

In a study of the relative effects of copper and galvanised piping on the growth of taste-producing actinomycetes and fungi in pipes, Windle Taylor (59) found no difference, fungi growing equally well in both types of piping. Slimes which grow in water exposed to an alcoholic atmosphere and normally attributed to fungi, as these form the bulk of the material of the slime, were also investigated (59). The primary invader was shown to be a bacterium derived from the water, followed by protozoa and the fungi appeared later.

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## **LARGE-SCALE TISSUE CULTURE (P. D. Cooper, B.Sc., Ph.D.)**

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'LARGE-SCALE' tissue culture has in the last decade become feasible in considerable measure because of the impetus derived from poliomyelitis virus vaccine production, and doubtless this new field of industrial enterprise will continue to grow, as its commercial potentialities are world-wide. However, tissue culture on a scale even approaching modern full- or pilot-plant-scale operation is so recent, and differs sufficiently from usual microbiological processes, that the trends cannot well be discussed without some introduction to the methods of tissue culture. The differences fortunately are not fundamental but quantitative, as animal cells in the free-living state behave as true micro-organisms.

### **Definitions**

'Tissue culture' implies the growth or maintenance of cells derived in the first place from an animal (nearly always a vertebrate) or a plant, in a living form apart from the organism of origin. Its history for tissue pieces extends back to the early 20th century. However, 'tissue' is nowadays often a misnomer, since the tissue as a whole is not kept, but only certain cells from it; hence strictly speaking one should refer to 'cell culture' or 'organ culture', although 'tissue culture' is still frequently used. While considerable data are now available for cell culture, organ culture is still in its infancy and will not be dealt with here; generally speaking organs can be maintained but not grown in culture, and the first problem to be solved is to prevent the organ from disintegrating by the migration and dispersal of its cells in culture.

### **Principles of cell culture**

Earlier, cell culture was extremely difficult, and three developments of the last 15 years have contributed to making it much easier: (a), by far the most important, the advent of non-toxic antibiotics to prevent microbial contamination; (b) standardisation and ready commercial availability of synthetic medium components such as a wide range of vitamins and amino-acids; and (c) availability of quantitative methods for evaluating cell growth, i.e., free-living, single-cell suspensions which are reproducible, easily sampled in a representative fashion and accurately counted. These factors allowed the systematic investigation of culture

conditions, and many techniques and fully or semi-synthetic media are now available for a variety of tissues.

For general techniques reference is made to a recent text-book of cell culture (1), but it will be useful here to summarise the differences of animal cell culture from standard microbiological technique, since advances in large-scale cell culture all stem from realisation of and allowing for these differences. They centre around the characteristics of the cells, which compared with bacteria are (a) much larger and heavier, although of similar density (and hence require more diligent agitation), (b) very much more fragile mechanically, and thus more readily damaged by agitation procedures, (c) much more susceptible to adverse chemical environment, (d) much more slow in growth (doubling time 12-48 h.). Consequently care has to be taken in their handling—they are damaged by grinding, too rapid stirring, sparging, frothing, certain but not all antifoam agents (2), too rapid centrifuging, keeping as a packed pellet, and incubation in acid (pH 6.5), alkaline (pH 8.0) or deficient media. Pumping in bulk requires special pumps such as those used for pumping whole blood. Also unlike bacteria, the cells prefer to attach themselves to solid objects, and consequently tend to clump or adhere to the vessel wall. However, on the credit side they are sedimented by low centrifugal forces and require a lower rate of oxygen input and acid removal.

### Culture medium

The medium is also more complex and critical than those required for micro-organisms, and much more costly. This latter factor has been justifiable economically hitherto, because the products (virus vaccines) were relatively rare and are used in small doses, but more efficient vaccines demand higher doses; fortunately considerable scope exists for cheaper substitutes, for example use of skim milk in place of serum, and tryptic meat broth (3) in place of amino-acids or purified hydrolysates. Continuous cell lines may be developed which are independent of added protein and otherwise nutritionally less demanding. With adequate control, the expensive but very useful antibiotics might be omitted or used in lower dose. The medium needs to be isotonic with the correct balance of salts (4), with about thirteen amino-acids (5) (more than the seven required *in vivo*) and about seven vitamins (6) plus protein. The pH needs to be about 7.0, and the oxygen tension may be critical (7). There is now a very extensive literature indeed on tissue culture methods in general and in particular.

### Cell source and methods of culture

There are three sources of cells for use in tissue culture, all suitable for large-scale application. The first and that entirely used

commercially so far is the intact animal, either from a part thereof (e.g., kidney) or the whole animal, usually an embryo (e.g., chick). Embryo cells are more easy to cultivate than adult tissue, and are frequently more sensitive to viruses. The organ is removed and coarsely chopped or minced; it can be used as this crude suspension of cell clumps (the first means used to make polio-virus vaccine), but better results are obtained by digesting the tissue with trypsin to obtain a single-cell suspension which can be maintained, usually as a single layer attached to a glass surface (monolayer) or as a suspension. Primary cultures do not increase greatly; they may be subcultured once or twice (giving secondary or tertiary cultures) but then usually expire. Primary cultures have the advantage of being less liable to loss by bacterial contamination, but suffer the disadvantage of frequently being contaminated with wild viruses.

The second source is that of the continuous cell lines, which have all resulted from infrequent successes in attempting to subculture primary cultures indefinitely; these successes occur sufficiently often to make it feasible to obtain almost any primary culture in a form capable of indefinite subculture, although certain types of cell are more difficult (8), and the resultant cultures may not necessarily have the same characteristics as the primary source. They are grown either as monolayers or in suspension.

The third source is the peritoneal exudate of certain ascitic tumors (9) which, while not strictly tissue cultures, nevertheless yield cells directly in a suspension eminently suitable for culture work. This source is in fact so bountiful (e.g.,  $1-2 \times 10^9$  cells per mouse in 10 days) that it is surprising that more use is not made of it.

### Principles of large-scale cell culture

Large-scale tissue culture of indefinitely cultivable cell lines is at present at a stage similar to that of penicillin fermentation at the time when deep culture was first introduced. The analogy is fairly close; the bulk of current commercial tissue culture is at present performed with the cells growing as monolayers, which are handled in separate flasks, as were the penicillin surface cultures. However, the same cells will in general also grow well in a shaken suspension if the right conditions are employed (10), and the system has been reduced to the simplified 'stirred pot' by McLimans and co-workers (11). This has been employed experimentally on a variety of scales up to several litres (12, 13) in batchwise growth and commercial exploitation is being investigated. Batch cultures are not efficient, however, since the optimal conditions for growth of animal cells are critical and are soon exceeded in culture; it would therefore be preferable to maintain the cells in a steady state under optimal conditions, with an apparatus analogous to a chemostat. Such an



apparatus has been successfully operated over periods of many months, and produces  $10^9$  cells per day from a 1.5-l. culture volume (14). This method would be very much more economical for vaccine production than is, for example, obtaining cells from the expensive monkey kidney, and even for cheaper tissues (e.g., pig kidney cells) the amount of handling is much simplified. The prime need is to obtain a strain of cells which is capable of indefinite subculture, yet which possesses the desirable characteristics of the primary cells (such as sensitivity to the particular virus needed for a vaccine).

### Uses of large-scale cell cultures

Tissue culture on a large scale has at least two uses, one for production purposes and the other for diagnosis and research. For the latter, advances in modern medicine have given tools to the microbiologist for the isolation, identification and assay of a large number of hitherto unknown viruses; these methods frequently depend upon cells in culture, but their production in bulk and variety is tedious and time consuming for the diagnostic laboratory. In America the production and shipping of large quantities of such cells on a commercial scale is a routine matter. Knowledge of the cause of a virus infection should increasingly help treatment and epidemiological handling, and in the years to come rapid diagnosis may become essential, implying a greater need for these cells all over the world.

The main use, however, is for production, and the main products are virus vaccines. The observation of Enders and co-workers that polio virus (a neurotrope) could grow in non-nervous tissue *in vitro*, launched the present polio virus vaccine industry, which has grown to a large investment in most industrialised countries, large and small. The virus is grown in monolayers of monkey kidney cells, and inactivated with formalin for injection; alternatively a living but attenuated strain can be given orally. It is likely that other vaccines for minor human ailments (measles, certain respiratory infections) will follow, but the number of monkeys available is limited. Considerable thought has been given to overcoming this limitation by use of continuously cultivated strains of cells, but these cells have many of the characters of malignant cells, and it is feared to administer an extract of such cells to humans even if it is purified chemically and thoroughly inactivated. This objection does not apply to livestock, and it is anticipated that in time a large variety of animal virus vaccines including foot-and-mouth disease virus, will become available by means of continuously cultivated cells, perhaps grown in a chemostat.

A variety of other uses can be envisaged. Production of hormones by rare tissues is an obvious one which in some unpublished work

has been successful, and connected problems may be the maintenance of large organs in culture for the same purpose, or for surgical grafting. The difficulty lies in obtaining a cell which performs as well *in vitro* as *in vivo*. The physiological behaviour of animal cells in a large compact mass (e.g., as an organ) is rarely the same as when in disperse culture. Although this presumably relates to the chemical environment, the reasons for it are not known and bear on the general problem of morphogenesis and differentiation; the cells appear to 'de-differentiate' in culture, perhaps by loss of some stimulus or control *in vivo*, or because only unspecialised cells survive in culture.

While this article has been concerned largely with culture of animal cells, it should not be forgotten that plant cells can also be cultured in a somewhat similar fashion. It would hardly be economical to do so for foodstuffs, but might be considered for rarer substances, such as drugs produced by tropical plant tissues, in order to avoid costs of transport or difficulties of access.

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## MICROBIOLOGY OF THE SOIL (Margaret E. Brown, Ph.D., and R. Cooper, D.Phil.)

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THIS review deals mainly with nitrogen transformations by soil organisms. After years of slow progress, knowledge of the mechanisms of nitrogen fixation and nitrification is now increasing rapidly with the application of a greater variety of biochemical techniques; prospects for further advances are promising. Many nitrogen-fixing micro-organisms have now been described and their physiology and ecology studied. The complex relationship between plant and organism in the rhizosphere has been further unravelled and there are signs of reviving interest in the related subject of bacterial fertilisers, long neglected outside the Soviet Union. The organisms which attack insoluble phosphates in the soil and thereby increase the phosphate supply for plants have received more attention, and the recent findings are reviewed.

### Biological nitrogen fixation

Recent work suggests that a great range of organisms fix nitrogen. *Derxia gummosa* was as efficient as *Azotobacter*, fixing 9.21 mg. N/g. of carbon source supplied, but was more acid tolerant than *Azotobacter* (1). Others, which were less efficient and fixed amounts of nitrogen ranging from 1 to 6 mg./g. of carbon source supplied, were identified as *Achromobacter* spp. (2), *Desulphosibrio desulphuricans* (3) and a possible *Saccharomyces* (4). Some species of actinomycetes may fix nitrogen but active forms were rare (5).

Many papers have dealt with the isolation of *Azotobacter* from widely differing habitats. In New Zealand, however, it was not detected in some soils of natural fertility under tussock, crops or introduced pastures (6). Russian workers claim that good cultivation, the regular application of organic and mineral fertilisers, and irrigation favour the growth of *Azotobacter* (7, 8). Evidence for the stimulation of *Azotobacter* in the rhizosphere is conflicting; some plant species depressed it and others stimulated early in the plant life, but depressed it later (9, 10).

For many years there have been reports of increases in soil nitrogen of the order of 50 lb./acre/year in both cultivated and uncultivated soils without legumes. A possible explanation is that some non-nodulated plants may fix considerable amounts of nitrogen (11). Plants grown for 6 months to 3 years in sand culture free from combined nitrogen and without *Azotobacter* and *Clostridium* showed gains in nitrogen; the results were confirmed by  $^{15}\text{N}$  analyses. The nitrogen may be fixed by specific plant and microbial associations, such as mycorrhiza or bacteria in stipular glands.

#### *Mechanism of nitrogen fixation*

Advances in knowledge of the mechanism of nitrogen fixation have been delayed until recently by failures to demonstrate consistently high activities of nitrogen fixation by cell-free extracts. This problem has now been overcome, and fixation was demonstrated with cell-free extracts of *Clostridium pasteurianum* when experimental conditions during and after disruption of the cells were carefully controlled; in particular, it was necessary to exclude oxygen and to supply a source of energy. Pyruvate was the most effective energy source of those tested, probably because it participated in the phosphoroclastic reaction, which is important for the supply of energy in some clostridia (12, 13).

Cell-free extracts fixing nitrogen have now been obtained from *Cl. pasteurianum*, *Rhodospirillum rubrum*, blue-green algae and *Azotobacter vinelandii* (14-16). In some of the experiments with *Azotobacter*, a significant advance in tracer technique was made by the use of  $^{13}\text{N}$ , a radioactive isotope with a half-life of only 10 min. (16).  $^{13}\text{N}$  may be better than  $^{15}\text{N}$  for very-short-term experiments because it offers greater sensitivity with smaller amounts of labelled material and its assay is less laborious.

The first step in the uptake of nitrogen from the atmosphere by nitrogen-fixing organisms is still unknown. Nitrogen specifically changed the absorption spectra of cell-free preparations from *Cl. pasteurianum* and soya-bean (13, 17). The weight of evidence from work with various organisms still suggests that nitrogen is reduced at a very early stage, possibly to hydrazine or some related compound (17-20). It is still possible, however, that nitrogen is

initially oxidised (21); nitrate reductase and nitric oxide reductase were very active in tissues and organisms which could fix nitrogen (22, 24). Ammonia remains the first identified product of nitrogen fixation (14, 16);  $^{15}\text{N}$  taken up by extracts of *Cl. pasteurianum* appeared quantitatively as  $^{15}\text{NH}_3$  (13). The earlier report (18) that cyclic compounds from the condensation of  $\alpha$ -ketoglutarate with hydrazine behaved as intermediates between nitrogen and ammonia in *A. vinelandii* remains unconfirmed.

A timely warning to those using isotopic tracers in studies of nitrogen fixation comes from the report that a mutant of *A. vinelandii* incubated with  $^{15}\text{N}_2$  exchanged nitrogen with the atmosphere without net fixation (25). Such exchange reactions may lead to an isotope distribution different from that produced by fixation.

#### Root nodules

The complex and intimate symbiosis between plant and microbe in the root nodules of legumes and certain non-legumes, leading to massive increases in nitrogen in the soil (cf. 26), has had further detailed attention. The production of nodules by legumes is influenced by light and by combined nitrogen in the soil; both too low and too high a carbon/nitrogen ratio inhibited nodulation, and different legumes were differently affected by a given set of conditions. Carbon and nitrogen compounds at the sites of nodulation were also important (27). The initial nodulation of seedlings of lucerne and red clover was delayed by small amounts (20  $\mu\text{g}$ . of N per seedling) of nitrate or nitrite, but not by ammonium ions, asparagine or urea (28).

An explanation for the specificity of cross-inoculation groups—the nodulation by a given strain of *Rhizobium* of a limited range of closely related legumes—comes from the report that the specific *Rhizobium* induces the root to produce enzymes that break down pectins, whereas non-specific strains do not (29, 30).

The idea that *Rhizobium* invades the root hairs of its host by causing invagination of the cell walls has gained support from direct observations of various legumes (31). Such invasion may produce nodules effective or ineffective in nitrogen fixation; the genetic differences in red clover responsible for the different types of effectiveness have been analysed and summarised (26). Ineffective nodules lack haemoglobin, probably because they lack enzymes of porphyrin biosynthesis (32).

Some recent valuable work on the processes leading to nitrogen fixation in mature nodules of legumes arose out of the earlier demonstration that the bacteroids which fill the nodules are in packets surrounded by membranes, probably of plant origin. When detached nodules of soya-bean were exposed to  $^{15}\text{N}_2$  for short periods, the greatest enrichment of  $^{15}\text{N}$  was in the membranes and none was detected in the bacteroids (33). The main function of the

bacteroids may be to reduce haemoglobin, which may in its turn reduce the nitrogen fixed at the membranes (17, 20). The possibility that haemoglobin may itself act as initial acceptor of nitrogen arises from the demonstration of a weak affinity between haem proteins and nitrogen. At equilibrium, the proportion of nitrogenated molecules was small, but the high molar concentration of haemoglobin in root nodules is probably large enough for active uptake and transfer of nitrogen (34, 35).

The increasing knowledge about nodules of non-legumes has been reviewed (36). Until recently, evidence for the isolation of symbiotic microbes from such nodules was poor, but now a virulent organism from nodules of alder has been grown slowly on a medium containing an alcoholic extract of alder root (37). Another organism, growing rapidly on ordinary media and claimed to be an actinomycete, was isolated from the same host (38). Nodules of legumes and non-legumes show important similarities in their fixation of nitrogen, especially in the effects of inhibitors (39, 40), but haemoglobin is more firmly bound to the nodule tissue in non-legumes than in legumes, and escaped detection until recently (41).

### Nitrification

The bacteria oxidising ammonia or nitrite in soil are notoriously difficult to handle and are slow in growth; nevertheless, techniques for their culture continue to improve. *Nitrosomonas europaea* has now been grown in continuous culture, yielding gramme quantities of dried cells, deep red in colour from their content of cytochrome. A strong supply of air is essential for rapid growth (42).

The ability of cell-free extracts to perform some of the reactions of nitrification is beginning to yield useful information. The coupling of phosphorylation to the oxidation of nitrite to nitrate in a particulate preparation from *Nitrobacter agilis* indicates how this organism derives its energy from nitrification (43, 44). A cell-free extract from *Nitrosomonas europaea* oxidised hydroxylamine, but not ammonia, to nitrite (45). Gas exchanges during nitrification, and the effects of pH and various inhibitors, were studied with whole cells of *Nitrosomonas* and *Nitrobacter* (46-48).

### The rhizosphere

The rhizosphere, the region of soil influenced by plant roots, is characterised by having greater microbial activity than soil away from the roots. Germinating seeds stimulated bacterial growth (49) and the rhizosphere effect was initiated early in plant life; there were more than twice as many bacteria in the rhizosphere of 3-day-old wheat seedlings as in soil away from the roots (50). Certain groups of organisms, such as chromogenic and Gram-

negative forms, which include proteolytic types, ammonifiers and methylene blue reducers, are stimulated in the rhizosphere (51, 52). Gram-negative bacteria may be favoured in the rhizosphere because they can grow well in the anaerobic conditions which may develop there (53).

The rhizosphere microflora is ultimately influenced by the environment in which the plant is growing because light and temperature affect exudation from roots; with increase in temperature the amount of exudate increases. When tomato, *Phalaris* and clover were grown under controlled light and temperature, tomato and *Phalaris* exuded greater amounts and different proportions of amino-acids than did clover (54). The rhizospheres of wheat plants receiving 1000 foot-candles of light had more bacteria, especially those able to ferment glucose, than plants receiving only 300 foot-candles (55). These experiments stress the importance, for reproducing results, of growing plants under controlled conditions.

Further analyses of root exudates from wheat (56) showed them to contain volatile and non-volatile organic acids, amino-acids, sugars and traces of nucleotides, but none of the group-B vitamins.

Root exudates can affect the behaviour of plant pathogens. When *Fusarium oxysporum* f. *pisi* was close to the root surface it was usually stimulated by root exudates, but sometimes inhibited by other rhizosphere micro-organisms. Roots did not become infected until the exudates stimulated the fungus enough for it to withstand the antibiosis (57).

In addition to root exudates affecting the rhizosphere flora, there are also microbial exudates affecting the roots. Rhizosphere micro-organisms produced vitamins of the B group, high concentrations of which were found in cultures of non-sporing bacteria, particularly *Pseudomonas* species (58, 59). Heteroauxins were produced by *Pseudomonas* species and *Fusaria*, and culture filtrates of *Fusaria* made the roots of 3-day-old rice seedlings elongate (60). In clover grown in sterile culture and inoculated with a soil suspension, the main root was shorter and root hairs, particularly those near the root tip, were shorter and fewer than in uninoculated plants (61).

#### Phosphate-dissolving micro-organisms

A study of the distribution of phosphate-dissolving micro-organisms in light chestnut soils in Russia (62) showed the presence of few in uncropped soil but many on the roots of several crops, and the numbers varied with plant age; *Pseudomonas calcis* predominated. However, in other experiments, these bacteria were not preferentially stimulated on the roots of wheat and oats (63, 64). Phosphate-dissolving micro-organisms were increased by adding rock phosphate to soil. *In vitro* these organisms were more active in the presence of organic matter (65).

Many of these bacteria produce organic acids; lactic acid is common and 2-ketogluconic acid has also been identified. The liberation of soluble phosphate from insoluble calcium phosphates by these acids may be related to their strong chelating power towards calcium (66, 67). Actively growing fungal hyphae also produce organic acids and grow chemotropically towards particles of rock phosphate, finally surrounding them with a mycelial network (68). Phosphatases are also thought to liberate unavailable phosphorus from organic compounds (69). Species of *Aspergillus* contained especially active phosphatases, and a phytase which could dephosphorylate ferric phytate, a compound previously considered almost inert in the soil. Because these enzymes are most active at low pH they are likely to be active in the more acid soils where fungi are abundant (69).

### Bacterial fertilisers

Most of the published work on bacterial fertilisers has come from the Soviet Union, where preparations of *Azobacter* spp., of *Bacillus megaterium* var. *phosphaticum* and of *Rhizobium* spp. (for which Russians use the terms azotobacterin, phosphobacterin and nitragin, respectively), are applied as standard farm practice over about 25 million acres. Present-day theories and practice have now been reviewed (70) and the increasing number of translations of Russian journals should help English readers to keep in touch with future developments.

Azotobacterin and phosphobacterin were said to benefit 50-70% of the field crops to which they were applied. Increases of up to 20% in yields of cereals (71), tobacco (72), tomato (73), cotton (74) and sugar beet (75) were claimed. Bacterial fertilisers are effective only when used in a favourable soil, such as a rich humus loam of neutral pH; manuring also favours *Azotobacter* (76). *Azotobacter* strains isolated from the local soil gave better results than standard laboratory strains (77), and their ultimate beneficial effect increased when the strains were first adapted to the crop by repeated subculturing in the presence of the respective plants grown in sterile culture (78). The combination of azotobacterin and phosphobacterin was sometimes more and sometimes less effective than the application of either fertiliser separately (72, 79).

Other micro-organisms are thought to be as good as or better than *Azotobacter* for use as bacterial fertilisers, and *Pseudomonas* spp., particularly *Ps. fluorescens* (80), and *Clostridium pasteurianum* (81) have received attention.

In addition to increasing crop yield, all these fertilisers may affect the crop food value and the activities of certain plant enzymes (70).

The mechanism of the action of bacterial fertilisers other than nitragin is uncertain. There is little evidence that the benefit of



azotobacterin comes from nitrogen fixation (70); the production of 'growth-promoting substances' is put forward as an alternative hypothesis (73). Various micro-organisms produce vitamins and indolylacetic acid which may affect plant growth. Alternative or additional effects of 'fertiliser' organisms may be the destruction of soil toxins, antagonisms towards phytopathogens, or the conversion of plant nutrients in the soil from unavailable to available forms (70).

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**CHEMICAL ENGINEERING Etc.**





## HEAT TRANSFER, FLUID FLOW, UNIT OPERATIONS, Etc.

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### Unit operations

#### *Diffusion and mass transfer*

In the present period much attention has been paid to the fundamentals of mass transfer processes, the usual method of attack being the measurement of the rate of dissolution of materials in fluid streams (1). In investigations of this type Pasternak & Gauvin (2) introduced a new dimension into the Reynolds number, the use of which is explained by boundary layer theory. The effect of rippling and turbulent flow on mass-transfer rates is very difficult to treat theoretically, but some advances have been made recently and are reviewed by Enlford (3) with special reference to foreign publications.

Mass transfer between vapour bubbles and liquid in nitrogen-oxygen mixtures has been investigated (4). This type of investigation is of importance in the examination of distillation and absorption fundamentals in plate towers.

A review of recent developments in the field of thermal diffusion is published by Brown & Jones (5). It is stated that commercialisation of the process may soon be effected.

### Absorption

A review of the classical theories of absorption by Carter (6) includes some recent work. A recent development of general interest is outlined in a paper (7) dealing with the employment of concurrent flow in absorption units. High mass-transfer coefficients have been obtained in experiments with carbon dioxide and alkaline solutions and the system may be used to advantage when vapour pressure over the liquid is low. The problem of assessing the size of equipment when absorption is accompanied by chemical reaction is considered by Tiller (8), who discusses the suitability of the various theories of absorption. The materials used in the construction of absorption equipment have been considered by Hilliard (9), who describes the use of the 'Polybloc' system, a

graphite material, which has advantageous corrosion resistance and thermal properties.

The hydrodynamic conditions of absorber operation are considered in a paper by Eduljee (10), with a review of correlations of flooding, loading and pressure drop in packed towers. A new correlation is proposed to cover a range of liquids and gases with improved results.

### Distillation

An international symposium on distillation was held this year at Brighton and a review of the papers presented is published in *British Chemical Engineering* (11).

The increasing application of the computer in the field of process design is seen in several papers (12-14). Binary mixtures of ideal, non-ideal and azeotropic characteristics and multicomponent designs have been analysed. The rapid assignment of new conditions after an unsuccessful pass through the tower is described.

Azeotropic and extractive distillation have also claimed attention. A review of new techniques in the separation of azeotropes is published by Coates (15). The choice of separating agent and column design for extractive distillation is examined by Gerster (16), who has also detailed new methods of distillation tray efficiency prediction (17).

In the more fundamental aspects of the subject some recent research work (18) seeks to discover how the material properties of a substance to be rectified affects the exchange relationship or column height.

### Extraction processes

The present state of extraction processes in the oil industry is reviewed by Fenske (19) and the pattern of the future use of the process is predicted.

In the analysis of extraction processes several new methods have been proposed. The simple McCabe-Thiele type of construction for immiscible solvents has been extended (20) to include other cases. A new method of determining tie lines in ternary systems (21) may be employed in the absence of adequate chemical analysis, and its use is illustrated by the system acetic acid-furfural-water. An increase in mass-transfer rates in liquid-liquid extraction has been effected by the application of ultrasonics (22). The increase is regarded as being due to increase in interfacial area and removal of pockets of stagnant liquid.

### Drying

Heat- and mass-transfer in drying processes continue to be investigated, the emphasis being on spray drying (23). Some

aspects of dryer design have been examined and methods outlined for determining the residence time of material in the various zones of a dryer (24).

### Particle dynamics

In the field of particle dynamics work has proceeded on filtration, centrifugation, separation of dusts from gases and froth flotation.

The question of filtering media is discussed by Kovacs (25). The replacement of the old type of filter cloth, which is frequently unsatisfactory, by the impregnated cellulose screen, wire cloth, fused metallic fibre and other media is considered. The pre-treatment of slurries and the removal of the final filter cake is discussed by King (26), who outlines the latest developments in the fine chemical industry. A simple and cheap device for classifying solid particles, the hydrocyclone, is described by Gundelach & Trawinski (27). Various examples of its use in conjunction with other items of plant such as filters, thickeners and centrifuges, are cited.

In the field of froth flotation, some attempt has been made to investigate fundamentals. The adhesion of a spherical particle to a liquid/air interface has been investigated by Nutt (28), who developed equations for the force and work required to detach the particle from the interface. Results obtained agreed well with theory. New developments in centrifuging and its application in many industries are described in a comprehensive review (29).

### Mixing

Mixing processes can be divided into two categories, (i) the mixing of batches of material, and (ii) the mixing of different elements of material in flow reactors, as a function of time. Several reviews of processes falling into the first category have been published (30-32). They concern liquid/liquid systems, solid/liquid systems, pastes and dough mixing, and theory, practice and economics are considered. In the second category residence time studies in various types of equipment have been made (33, 34). Cholette (35) considered the problem of chemical conversion in flow reactors with differing orders of reaction and proposed graphical solutions.

### Size reduction

No new theories of size reduction have been reported. Comminution in jets has received some attention (36), while the fundamentals of this process have been investigated by Reiners (37) using a spark photography technique. The possibility of deriving a law for impact comminution is mentioned. Several new types of

mill have been developed which are of interest to the specialist reader and are referred to in the Supplementary Bibliography.

## Heat transfer

### *Design*

Nomograms continue to be published for the quick solution of many problems. A chart for the determination of the effective length of U-tube heat-exchangers, if the length and size of the tubes are known, has been published by Whitely & Ludwig (38), or the number of tubes may be determined if an effective length is assumed. A nomogram for the solution of unsteady-state heat-transfer problems in batch operations has been published by Narsimman (39).

The selection of heat exchangers for a particular duty is considered by Drake & Carp (40), in an article designed to allow users to benefit from manufacturers' 'know how' in their selection. Mechanical and economic factors are summarised in a table. The use of the digital computer in the selection of heat exchangers has been described (41) with a sample programme.

Evaporation has been considered as a special case of heat transfer in the Chemical Engineering refresher series (42). Characteristics of various types of equipment and the influence of physical properties of the solution on the heat-transfer coefficient are discussed.

New techniques in cooling tower technology have been reported from Germany (43). Ultra-light tower packings have been introduced with reported increase in mass transfer rates.

### *Research*

Two articles of general interest (44, 45) have been published by Birmingham University, covering the life and work of Schmidt and Nusselt, two prominent workers in heat transfer.

Two papers on the subject of unsteady state heat transfer have been published by Davies & Akers. An analysis of the process is based on the first law of thermodynamics, systems having variables based on time only (46a) and heat conduction in the solid phase (46b) being considered. In subsequent papers Davies (47) considered problems too complicated for analytical solutions. The solution of first-order differential equations is outlined and more practical problems tackled by solving simultaneous first-order differential equations. The use of numerical analysis to solve partial differential equations is also demonstrated.

Considerable interest in two-phase flow and the problems involving heat and mass transfer is demonstrated by the large number of papers on this topic presented at the 3rd American

National Heat Transfer Conference which are reviewed by Collier (48).

Heat-transfer studies between particles and liquid in a fluidised bed have been made by Sunkoori & Kaparthi (49). Many studies have been made previously on gas fluidised beds and the results from these experiments are compared with those from the liquid fluidised bed.

## Fluid flow

### *Fundamentals*

A recent development is the use of water analogues to determine dynamic gas flow patterns by use of tracer particles in the water streams (50). Possible applications of the method are outlined. In similar work by Suckling (51), flow patterns around naphthalene pellets, of oblate shape, were investigated with red ink tracer. Compared with spheres, separation occurred earlier and an explanation was presented.

Application of boundary layer theory to power law pseudo-plastic fluids has been performed by Schowalter (52), who developed two- and three-dimensional equations.

In the study of compressible fluid flow, ideal gas behaviour is often assumed but deviations become pronounced with increase of pressure. A method has been developed (53) which enables the critical velocity of any real gas to be calculated with ease and accuracy, using recent thermodynamic developments. A generally acceptable correlation of the influence of voids on pressure drop in a packed bed has been developed which agrees well with experimental results (54). Density fluctuations in fluidised beds indicate that bubbles grow from the dense-phase mixture or continuous capture of tiny bubbles (55). A  $\gamma$ -ray absorption technique also indicated that the gas velocity in the dense phase was very close to minimum fluidising velocity.

### *Pumping*

Pumping theory is outlined by Scriven & Rhodes (56) and the common classification of pumps into kinetic or positive displacement devices is extended. The theory of operation of the major classifications is considered and illustrations are provided of how basic theory is applied to obtain some of the familiar but specialised types of equipment.

Selection of pumps for the chemical industry has been considered by Hoffman & Calkins (57) and Gillmor (58). Corrosion resistance, flow rate, operating temperature and pressure, environment and fluid properties are some of the factors examined. An interesting development is described by Eck (59) in which an oscillating impellor is employed in a centrifugal pump with the

blades describing a straight path. A vortex at the centre of the impellor controls the flow.

### Metering

The use of quarter-circle orifices for flow measurement has been investigated by Landstra (60). Constant flow coefficients were obtained over a very wide range of Reynolds number even at very low flow rates. Experimental work was described and the manufacturing technique detailed. A useful new flowmeter has been constructed (61) which is similar to the rotameter but does not require a tapered tube. The apparent weight of the float is made to vary by attaching a chain.

A lay-out eliminating errors in manometer readings in the measurement of two-phase flow is described by Wicks (62).

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## INDUSTRIAL HAZARDS

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BROADLY, industrial hazards may be grouped under three heads: (a) those always present in any works where machinery is used; (b) those due to the manufacture or handling of chemicals; (c) fire or inflammable materials.

The Annual Reports of the Chief Inspector of Factories for 1958 (*1a*) and 1959 (*1b*) give clear pictures of the position in Great Britain. In the former, attention is drawn to the dangers arising from large-scale production and use of organic peroxides; chapters on nuclear energy and ionising radiations and on fire prevention are also included. The latter describes a revised method of reporting accidents as from 1st January 1959, whereby more informative and detailed analyses may be made. This report also shows that 'Handling Goods' is the largest single category (26%) of all accidents in factories in spite of the increasing use of mechanical handling devices.

Hazards due to the manufacture and handling of chemicals on a large scale include poisoning by inhalation and by contact with the skin. In small organisations the remedy is largely a matter of good housekeeping, but there are a number of well-known substances which under some circumstances can be very dangerous, e.g., chromium oxide, acetone and calcium hypochlorite (*2a*). With larger organisations there is the added risk of plant failure, and American literature is quite eloquent on this subject, as seen in a series of articles (*2b-d*) dealing with suggested safeguards. In this country questions of health hazards are fully dealt with in the Annual Reports of the Chief Inspector of Factories on Industrial Health for 1958 and 1959 (*3a, b*), from which it appears that beryllium, either alone or alloyed with copper, is still a powerful and insidious cumulative poison and that steroid therapy has produced encouraging results. Brooks (*4*) gives an account of practical experience in monitoring beryllium at Harwell. Some small but significant items are noticed in the report for 1958 (*3a*), e.g., revised treatment in cases of asphyxia, when administration of a mixture of 5% CO<sub>2</sub> in oxygen is recommended as a first-aid treatment for CO poisoning. In the 1959 report (*3b*) attention is drawn to the First-aid Boxes in Factories Order, 1959, which supersedes the

1938 Order and makes radical modifications in the statutory contents of first-aid boxes.

The continuing use of radioactive isotopes, the expanding application of X-ray examination of metals and plant and the increasing number of plants employing nuclear fuel has focused attention on the hazards of ionising radiations (4-6). Methods for removing radioactive particles from the air are described (6).

The special fire precautions needed when petroleum products or inflammable solvents are handled, are discussed by W. S. Wood (7), who covers the use, storage and disposal of inflammable solvents and includes a useful table of physical properties such as ignition temperature, flash point and inflammable limits for 22 solvents. Coleman (8) deals with the use of non-inflammable solvents as 'safe' diluents of inflammable liquids.

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## TOXICOLOGICAL HAZARDS

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### **The assessment of the toxicity of chemicals added to food**

RATHER than follow the pattern of previous chapters on toxicological hazards published in these Reports it has been decided to single out for discussion a topic which has been the subject of two official publications in this country during the period under review. This has been done because these documents will exert a powerful influence on the toxicological research carried out by industry and it is important that their contents should be widely appreciated.

Food is becoming increasingly contaminated by chemicals present as residues of insecticides, fungicides, etc., used to protect the crops from various pests and to preserve them during storage, or as substances deliberately added for various reasons during manufacture (1). It is inevitable that this contamination will become more widespread as a more determined effort is made to win the battle against hunger. Although the use of chemicals is necessary in man's struggle for more food there has been considerable public concern, much of it ill-informed, about the possible dangers to man and wild life which might result from these practices. Most concern has probably been expressed about the possible dangers to the consumers of the treated food, although the greatest risk in the case of pesticides is to the people who apply the chemicals.

The methods being used to safeguard the public, both as consumer and user, in the United Kingdom have recently been outlined in two publications (2, 3).

#### *Pest control materials*

The first of these describes an agreed scheme whereby manufacturers, importers, distributors and research workers outside industry, experimenting with chemicals for pest control which are to be used on crops intended for consumption, notify the appropriate government department (Ministry of Agriculture, Fisheries & Food) of new toxic chemicals and formulations which they propose to introduce into agricultural practice so that precautions for the correct use of these chemicals can be devised. This scheme,

which has actually been working for five years, puts into effect a recommendation of the Second Report of the Working Party on Precautionary Measures against Toxic Chemicals used in Agriculture (4). In addition to other information, each notification under this scheme must be accompanied by data on the toxicology of the substance so that the hazards to the users, consumers, farm stock and wild life (birds, mammals, fish and beneficial insects) can be assessed and adequate precautions agreed and recommended both officially and by the sellers. The toxicological information on the substance obviously forms a most important part of the notification and in an appendix to the main report the scope of the toxicological studies required is set out in some detail. A further appendix describes the scope of the residue data which is necessary to establish whether any of the chemical will remain in the food, i.e., the dose to the consumer.

It is, of course, impossible to lay down a scheme of routine tests for establishment of the toxicity of any chemical suggested for use in food production and which would give information on which a decision about its safe use could be based. The possible hazards arising from the use of a compound can only be determined by an intelligent consideration of the inherent toxicity of the substance, the proposed mode of use and its amount, state, etc., in the final product. It may be that the really relevant information about the toxicity of a chemical comes from a test far removed from those routinely employed in toxicological laboratories. Critical consideration of the results of the preliminary tests might well lead to an experiment of this type and save an enormous amount of further work. More research rather than more 'testing' is required in this field (5). While these points are recognised in the report, a certain minimum of investigation is laid down, based on previous experience.

In addition to a description of the relevant physical and chemical properties of the substance the notification of a new crop protection chemical must be accompanied by data on its acute toxicity, i.e., LD<sub>50</sub> values, determined by giving single doses of both the pure compound and its formulations by different routes to a number of species. The report emphasises that while the actual LD<sub>50</sub> value is useful for comparison with related compounds, it is much more important to describe the time course and symptomatology of the poisoning together with the post-mortem pathological findings. This is necessary because, for instance, compounds which produce irreversible damage to tissues such as the central nervous system could be more hazardous than substances with lower LD<sub>50</sub> which produce only transitory effects in sub-lethal amounts. It is known that one of the greatest dangers to the users of agricultural chemicals arises from contamination of the skin and subsequent absorption of the chemical into the body, and a considerable

amount of information is required about the percutaneous toxicity of the compound in addition to its effects on the skin itself. As well as these acute experiments the cumulative effects of known fractions of  $LD_{50}$  values over short periods and the effects of chronic exposure to the compound must also be determined. Delayed toxic effects must also be looked for in animals which have survived near-lethal doses. With some compounds, such as the organophosphorus insecticides, it is necessary to see if their effects are potentiated by other commonly used insecticides of this group. Organophosphorus compounds must also be tested on adult hens to see if they give rise to delayed neurotoxic effects. The hen is used in these tests because, like man, it is sensitive to the demyelinating action of some of these compounds. Metabolic studies can also be of great help in deciding on the potential hazards of a pesticide by showing that the compound is rapidly excreted, broken down to innocuous fragments in the animal body or is converted to a more toxic compound either in the treated crop or only after ingestion by the animal. Such data are required for notification together with information on methods of diagnosing poisoning by the compound and on possible therapeutic measures. The possible dangers of a compound can best be assessed when its mode of action is known, hence the need for a scientific inquiry rather than just a list of  $LD_{50}$  values, etc.

The above is merely an outline of the main headings of the section of the report dealing with the toxicological investigation of compounds proposed for use in agriculture and food storage and indicates the scope of the toxicological information required to support a Notification. The methods and species which may be used are discussed in some detail. Although the British Notification Scheme prescribes a detailed toxicological investigation of the compound it is more flexible than its United States counterpart (6) and pays rather more attention to possible user hazards. It is to be expected that from time to time further appendices will be added to the scheme dealing with such topics as the methods to be used to determine percutaneous toxicity and to assess the hazards to wild life from the use of agricultural chemicals.

It might be thought that this scheme will impose a serious burden on the industry which has to obtain all this information, but this burden is unavoidable in view of the large number of people at risk either as users or consumers.

#### *Carcinogenic risks*

The second publication (3) sets forth the conclusions of a panel of experts on the carcinogenic risks in food additives and pesticides. They concluded that no substance shown to be a carcinogen when given orally to animals should be added to or allowed to contaminate food. If such a substance is shown to be a carcinogen by



any other route of administration or if it attracts suspicion of carcinogenicity solely on clinical grounds, a scientific Standing Committee would decide whether it should be considered as a carcinogenic hazard to man if it became a food additive or contaminant. This Committee would keep the whole problem under review and would also advise on the best ways of testing compounds for carcinogenicity. As with the Notification Scheme, there is an appendix to this report giving guidance on the testing of materials for carcinogenicity.

Although this report was mainly concerned with consumer hazards, it is likely that the same considerations would be applied to user hazards. The user of the chemical, whether in field or factory, is much more likely to come in contact with toxicologically effective amounts of the chemical than the consumer of a food containing only traces of the added material.

The guide to screening tests for carcinogens given in this report does not aim to do more than enumerate the principles to be followed. In view of the diverse nature of the chemicals used in food preparation and agriculture a detailed scheme of testing, equally applicable to all, could not be laid down. The experiments must always be planned after appraisal of those which have already served satisfactorily for testing related compounds. With this in mind the appendix contains a discussion of the species to be used. Rats and mice of both sexes are advocated for routine use, starting with groups of 25, so that at least 12 mice in each group will be alive after 20 weeks and at least 12 rats in each group after 2 years. There are no good short-term tests available for the detection of carcinogens and this means that the experiments must cover the greater part of the animal's life-span. The compound should be given for at least a year and the dose should be as high as possible without materially affecting the life-span of the animal. Both oral and parenteral routes of administration should be used. At the end of the experiment the animals must be examined as completely as possible, both macroscopically and microscopically, and if the incidence of malignant tumours is statistically significantly higher in the treated group than in the controls the compound must be considered a carcinogen.

The object of this work is to build up a list of 'Permitted Substances' which have been adequately tested from this point of view. There are, of course, food additives in current use which have not yet been tested sufficiently and the Panel has recommended that these should be examined during the next 5 years. This is presumably one of the tasks which will be undertaken by the new British Industrial Biological Research Association (7). Further research is also needed on the methods for detecting carcinogenic compounds. Most of our knowledge of chemical carcinogenesis has been built up from the study of powerful chemical carcinogens, the

effects of which can be easily demonstrated. It is perhaps an assumption that the same type of experiment is equally suited for revealing the presence of a weak carcinogen or that a chemical is not a carcinogen. The latter problem is the more difficult and is the one most frequently encountered in this field.

The need for further work on methodology is clearly shown by the differences between the screening tests suggested in the Ministry of Health Report (3) and those in a recent publication of the National Research Council of the United States (8). Whereas the differences between the British and American approaches to the toxicological examination of pesticides are largely differences in emphasis, those between the proposed tests for carcinogenicity are more fundamental (9). Among the tests recommended by the American authorities are feeding the material to dogs for 4 years and repeatedly painting it on the skin of mice. Only experience will tell whether such tests are useful for detecting human carcinogens.

### Conclusion

There is no doubt that the Notification Scheme for Pesticides and the Report on Carcinogenic Risks in Food Additives and Pesticides will lead to a big increase in the already considerable amount of work done on the toxicology of the chemicals used in agriculture and the food industry. This is necessary if the health of the nation is to be safeguarded. An effect of these schemes will be that the hazards which may arise from the use of these chemicals will be more completely assessed than those for many, if not all, of the other groups of chemicals encountered both by industrial workers and by the public. This is probably already the case. If these schemes prove successful an extension of this type of joint Government-Industry scheme to other industries using toxic chemicals can be envisaged. The success of any official scheme in this field will depend on its ability to adapt to changes in the climate of scientific opinion attendant upon the increase in scientific knowledge on the subject.

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## FOAMS\*

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### Introduction

FOAMS have been of particular interest in the last few years, partly on account of the rapidly increasing industrial uses: they have become increasingly important in rubber preparations (foamed latex) and in fire-fighting (1), in which they have the double advantage that the density of the aqueous medium is reduced by aeration and that the surface area is greatly increased (2). This enables the foam to float as a continuous layer on the surface of a burning organic liquid, preventing the evolution of inflammable vapours and presenting a large area for the absorption of radiant heat, which assists in cooling the surface and surrounding edges and consequently reduces vapour pressure.

A recent study (3) of mass transfer in foams suggests that there may be future developments in commercial foam columns for gas absorption. In absorption one of the most important rate-controlling factors is the area of contact between the gas and the liquid, and the large interfacial area in a foam, as high as 50 cm.<sup>2</sup> in 1 c.c. of foam, is about 50 times greater than in columns packed with Raschig rings. This advantage may be partly lost, however, unless the stirring within the foam is especially effective, because, as explained below, the effective viscosity of a foam may be rather high.

*Separation and purification by foaming* is becoming increasingly common. If a stream of gas is passed through a mixed solution, the more surface-active materials are preferentially removed in the foam (4). It is possible that proteins could be concentrated from biological fluids by this mechanism. Rigorous purification of sodium lauryl sulphate and lauryl sulphonic acid has been possible by foam fractionation (5). In these materials slight hydrolysis alters the surface properties drastically, on account of the liberation of lauryl alcohol, which is adsorbed about 1000 times more strongly than the parent compound. Purification to a required level of better than 99.99% can therefore be suitably carried out by foaming, the first fraction of the foam, which contains the lauryl alcohol, being

\* Arranged by Surface Activity Group

discarded. In the same way foaming of sodium oleate carries off preferentially the oleic acid formed by hydrolysis (6).

Other uses of foam separations are in the flotation of minerals and in the separation of organic and inorganic ions by surface-active agents. Anionic collectors for the latter separations include  $\alpha$ -sulpholauric acid; while, for separating dyes, cationics such as laurylpyridinium chloride and quaternary derivatives are used. With successive small additions of the cationic derivative to a mixture of dyes in water, a good separation of the dyes may be achieved in the foam (7).

### Factors determining foam stability

A foam can never be thermodynamically stable, since, once the sheet of liquid is ruptured, it must break into drops with a lower total surface area and therefore with a decreased free energy of the system. Nevertheless, although foams from pure liquids and gases are highly unstable (life of less than 1 sec.), suitable surface-active agents can stabilise a foam almost indefinitely. In considering the action of these stabilising agents, several factors must be considered (8), of which the most important in the early stages is the drainage of liquid from the foam, with consequent weakening of the structure. Some foams, even when most of the surplus liquid has drained away, may still be fairly stable, the air bubbles being separated by liquid sheets of thickness of the order 200–2000 Å. Stability now depends on the resistance of these thin liquid films to further thinning by chance shocks: if the lamella is thinned to about 50 Å, molecular forces of attraction cause rupture. Further, the foam stability is reduced by growth of the larger bubbles at the expense of the smaller, which occurs by diffusion of gas through the liquid films, because the excess pressure in a small bubble is higher than that in a large bubble. The latest views on each of the factors responsible for foam stability are now considered, assuming a certain mean bubble size. Long-range forces of attraction do not appear to be important.

#### (i) *Drainage rate*

The drainage rate is the rate at which liquid drains from a foam whose lamellae are not breaking during the process. Drainage occurs under the action of gravity or of surface tension; the latter process involves liquid being drawn into the plateau borders between bubbles. Foams of common detergents as well as those of proteins show considerable drainage of liquid, which reduces the stability of the foam considerably, by thinning the liquid sheets to such an extent that they are easily broken.

If  $V$  is the volume of liquid drained out of the foam after a

time  $t$ , the rate of gravitational drainage should be given (9) by

$$dV/dt = \frac{1}{2}BV_0(Bt+1)^{-3/2} \dots \dots \dots (1)$$

where the amount of liquid drained from the foam should approach  $V_0$  (the total amount of liquid in the foam) as  $t$  becomes large: this means that the amount of liquid held in the fully drained lamellae in the foam must be negligibly small. This equation involves only a single arbitrary constant, and fits diverse types of foam reasonably well. The constant  $B$  is clearly a measure of the initial drainage rate: the values of  $B$  found by comparison with experiment decrease markedly with increasing expansion and viscosity of the foam, as expected. Agreement of equation (1) with the drainage from a slower draining foam, for example that from protein hydrolysate, is better than that with the faster draining foams (see reference 8). This is to be expected in view of the assumption of infinite surface viscosity which was required in its derivation. The value of  $B$  varies approximately inversely with the expansion of the foam.

According to the theory used in the derivation of equation (1), the constant  $B$  should vary directly with  $\rho/\eta$ , the bulk density and viscosity of the liquid. Foams from viscous liquids, for example, should have low values of  $B$ , i.e., the drainage should be slow: experimental studies (10) of the average life of the liquid in the foam (proportional to  $1/B$ ) as a function of liquid viscosity and density confirm that there is a linear relationship with  $\eta/\rho$  for both oil foams and aqueous foams. The effect of the surface viscosity of the stabilising film is more complex: in deriving equation (1) it is assumed that the surface viscosity is always so high that the formula for the flow of liquid between stationary plates is valid, i.e., that the gas-liquid interface is effectively solid. This assumption appears valid for protein films, but not for detergent monolayers.

#### (ii) *Diffusion of air across liquid lamellae*

In a column of foam the small bubbles will tend to decrease in size, and the large bubbles to grow, because the gas pressure is higher in the smaller bubbles. The mechanism of transfer of air from the smaller bubbles to the larger is by dissolution in, followed by diffusion through, the liquid lamellae separating the bubbles. A good example is provided by a foam made from Teepol solution: after 15 minutes the total number of bubbles is only 10% of the initial number, although no rupture of the liquid films has occurred (11). This striking effect is caused by the rapid thinning of the liquid sheets in foams from Teepol and other branched-chain compounds, the rate of diffusion of gas through the liquid sheets varying inversely with the thickness of the sheet. Further, Kitchener & Cooper (12) point out that the growth of the large bubbles may be followed by mechanical rearrangements of the

bubble clusters, with the consequent possibility of mechanical shocks.

Experiments with single bubbles (13) have made possible measurements of the permeability to air of the liquid lamellae: recalculated values (8) are of the order  $10^{-2}$  cm. sec. $^{-1}$ , corresponding to diffusion through liquid films whose thickness ( $h$ ) is of the order 5000 Å. Drainage of the lamellae below this order of the thickness  $h$  is very slow in these experiments with single bubbles below a plane surface.

(iii) *Thickness of the electrical double layer*

If the lamella of liquid is bounded by two charged monolayers (e.g., of long-chain sulphate ions), it may resist further thinning below a thickness  $h_{\infty}$ , reached after long drainage. The electrical repulsion between the bounding monolayers may thus stabilise the lamella against moderate shocks.

Although  $\psi_0$  (the electrical potential of each monolayer) will determine the gas pressure required to reduce the lamella to any required thickness, as a simplification one may assume (14) that the mean thickness ( $1/\kappa$ ) of the ionic double layer associated with each charged monolayer determines the thickness of the lamella. Further, it is assumed that each ionic double layer extends (14) only to a distance  $3/\kappa$  into the liquid and that the lamella is under a relatively low excess pressure from the gas in the bubbles; this distance corresponds to a repulsive potential of only a few millivolts. Thus, at about 1 atm. pressure,

$$h_{\infty} \approx 6/\kappa + 2 \times (\text{monolayer thickness}) \dots \dots \dots (2)$$

For charged monolayers adsorbed from  $10^{-3}$ N-sodium oleate, the final total thickness ( $h_{\infty}$ ) of the aqueous layer should thus be of the order 600 Å (i.e.,  $6/\kappa$  or  $18/\kappa$  Å): to this is added 60 Å for the two films of orientated soap molecules, giving a total of 660 Å. The experimental figure (15) is about 700 Å. With NaCl added to a concentration of  $10^{-3}$  N, the estimated thickness is 490 Å (experimental about 420 Å); with  $10^{-2}$ N-NaCl the figures are 240 Å and 280 Å, and with  $10^{-1}$ N-NaCl these become 120 Å and 120 Å. For Aerosol-OT (dioctyl sodium sulphosuccinate) of ionic strength approximately  $10^{-2}$ N, the estimated thickness of the liquid film is 240 Å (experimental value = 240 Å) and, with  $10^{-2}$ N-NaCl present, 190 Å, which again agrees with experiment.

At higher values of the gas pressure the thickness  $h_{\infty}$  decreases below the values given by the above approximation; the  $h_{\infty}$  vs. pressure isotherms agree with the results expected from a full analysis of the diffuse electrical double layer (15).

(iv) *Surface viscosity and yield values*

In addition to reducing the draining rate, the surface and bulk viscosities cushion the thin liquid films against mechanical,

thermal or chemical shocks. For a given shock, the relative increase in the area where thinning occurs will be written  $j$ , and the above factors reduce this shock area. The highest foam stability is associated with appreciable surface viscosity and yield values, while solutions yielding foams of very poor stability show very low surface viscosity (13). Teepol and other branched-chain compounds have very low surface cohesion, and their foams show rapid thinning, whereas the materials of higher surface viscosity (potassium laurate and proteins) have longer drainage times.

Whether an enhanced surface viscosity is a necessary condition for foam stability, and, if so, what is the minimum requisite value, have yet to be decided. The sensitive 'surface traction' type of surface viscometer (8) would be necessary for studying the lower surface viscosity limit. Clearly, however, surface viscosity is not a sufficient condition for foam stability: cetyl alcohol gives highly viscous monolayers but does not stabilise foams.

(v) *The restoring effects of surface tension*

These were recognised by Marangoni (1871) and by Gibbs (1878): the stability of a liquid film must be greatest if the surface tension strongly resists deforming forces (16, 17). Suppose that (in spite of surface viscosity) some shock has suddenly extended the local area of the lamella by the factor  $j$ . This induces a surface pressure gradient to the thinned region from the rest of the surface, i.e., the monolayer tends to spread back into the extended region. If the latter is relatively small, the change of surface pressure  $\Delta \Pi$  is given for each of the boundary monolayers by

$$\Delta \Pi = - \left( \frac{\partial \Pi}{\partial A} \right) (A_2 - A_1)$$

where  $A_1$  and  $A_2$  are respectively the available areas per long-chain in the original and in the extended parts of the surface. Hence

$$\Delta \Pi = -A_1 \left( \frac{\partial \Pi}{\partial A} \right) \left( \frac{A_2}{A_1} - 1 \right) = -A_1 \left( \frac{\partial \Pi}{\partial A} \right)_t (j - 1) \approx C_s^{-1} (j - 1) \dots (3)$$

where  $j$  is the area extension factor as before. Note that the term

$A_1 \left( \frac{\partial \Pi}{\partial A} \right)$  is the surface compressional modulus of the monolayer,

denoted  $C_s^{-1}$ . For a large restoring pressure,  $\Delta \Pi$ , this modulus should be high. In the extended region the local reduction of the surface pressure to  $\Pi - \Delta \Pi$  results in a spreading of molecules from the adjacent parts of the monolayer (at a pressure  $\Pi$ ), to the extended region, the rate of increase of pressure in this extended

region being  $\left( \frac{\partial \Pi}{\partial l} \right)^{(\text{spreading})}$ . This differential will be increased by

low surface and bulk viscosities. The spreading of the adjacent

monolayers into the region extended and thinned by the shock will stabilise the lamella because the monolayers will carry with them a layer of the adjacent liquid (up to  $10^{-3}$  cm. thick), so opposing the thinning due to the shock. Evidently certain of the factors controlling foam stability oppose each other (18): a high liquid or surface viscosity makes the drainage rate slower, but once thin films have been formed, a high viscosity will delay transport of liquid back into a locally extended region. Further, during the time interval  $\Delta t$  the depleted monolayers in the extended region of the liquid film will partially replenish themselves by further adsorption from the adjacent liquid, increasing the pressure by

$$\Delta t \left( \frac{\partial \Pi}{\partial t} \right)^{(\text{adsorption})}. \text{ Although such adsorption will restore the}$$

surface tension in the thinned region, it transports no liquid to the

thinned area. Since the term  $\left( \frac{\partial \Pi}{\partial t} \right)^{(\text{adsorption})}$  is greater at high

concentrations of surface-active agent ( $\delta$ ), the lower foam persistence often observed at the higher detergent concentrations is thus explicable. An ingenious way of measuring the elastic properties of lamellae consists in forming these across the hair-spring from a pocket watch. The damping of the vibrating spring is a measure of the effect of surface tension changes and of the mechanical properties of the surface films (19).

### Summary of foam stability

For a foam of given mean bubble size (14)

$$\text{Stability} \propto f \left[ h, j, C_s^{-1}, \left( \frac{\partial \Pi}{\partial t} \right)^{(\text{spreading})}, \left( \frac{\partial \Pi}{\partial t} \right)^{(\text{adsorption})} \right] \dots \dots (4)$$

where  $h$  depends on the rate of drainage and hence on the surface and bulk viscosities and yield values, and after a long time reaches a limiting value  $h_\infty$  dependent on the ionic strength. For stability,  $h$  should always be as large as possible, to resist shocks and to reduce air diffusion from the small bubbles. The term  $j$  is the local extension ratio of the area of a lamella due to a given thermal or mechanical shock; it will be reduced, and the stability thereby increased, by high surface and bulk viscosities and yield values. The compressional modulus  $C_s^{-1}$  of the monolayers should, for stability, be as high as possible: this assists rapid flow of the monolayers (and some bulk liquid) into the extended region of the

lamella. This monolayer flow-rate is measured by  $\left( \frac{\partial \Pi}{\partial t} \right)^{(\text{spreading})}$ :

it should be as large as possible, which requires low surface and



bulk viscosities in addition to a high compressional modulus of the monolayer. The rate of adsorption, measured by  $\left(\frac{\partial \Pi}{\partial t}\right)^{(\text{adsorption})}$ ,

should generally be low, so as to allow time for spreading to occur; if, however, the lamella thickness is of the order  $h_{\infty}$  and spreading is very slow, a high rate of adsorption could thicken the extended region.

### Foam stabilising additives

If small amounts of lauryl alcohol are added to sodium lauryl sulphate, the foam produced is much more stable. Typical values are 70 min. for the life of a foam from pure sodium lauryl sulphate, and 825 min. with sodium lauryl sulphate containing 1% of lauryl alcohol. Lauric-isopropanolamide and other similar substances act in the same way (20).

Whether these foam-stabilising additives act by altering the surface viscosity and yield point of the adsorbed monolayers is thus of interest. The surface viscosities are low ( $10^{-4}$  to  $3 \times 10^{-3}$  surface poises), but they can be studied with the 'viscous-traction' instruments (8). With it, the effect on surface viscosity of very small amounts of additives can be studied in relation to foam life. A convenient solution for this purpose is 0.1% sodium laurate at pH 10 in distilled water (21, 22). Unlike laurate at lower pH values, this shows no appreciable foaming without additives, due to the fact that there is no lauric acid produced by hydrolysis at this high pH. The surface viscosity of this solution is too low to be detected, and the foam produced by intense hand-shaking lasts only about 3 seconds.

On the addition of very small amounts of foam-stabilising additives, in particular lauryl alcohol and lauric-isopropanolamide, the foam life increases drastically, with a concomitant rise in surface viscosity (22). The increase in foam stability occurs at about the same concentrations of additive as does the rise in surface viscosity. This suggests that at these low concentrations surface viscosity is a primary cause of the increased foam stability, but the very great stability at higher additive concentrations is not the result of a corresponding increase in surface viscosity: it may well result from high surface yield values and compressional moduli.

For a given increase in surface viscosity, lauryl alcohol is more effective in stabilising foam than is the amide, although smaller concentrations of the latter are involved. The isopropanol residue in the long-chain amide makes the latter more lipophilic, and hence more strongly adsorbed from solution, so that the amide is effective in molar concentrations only about one-third those of the alcohol; apparently the alkyl-amide group has no specific effect.

The stabilising effect of phosphate ions (21) on foams from laurate at pH 10 remains obscure; it may lie in the increased adsorption of long-chain ions at higher ionic strengths, or in the sequestering of traces of polyvalent metal ions.

### **Destruction of foam—foam 'breakers' or 'killers'**

These are substances which cause a local rupturing of the liquid film. They act by raising the surface pressure over a small region: from this region spreading therefore occurs, and as the film spreads it carries with it a layer up to  $10^3$  cm. deep. of the underlying liquid, thus thinning the film of liquid. This explanation, due to Ewers & Sutherland (23), shows the similarity in action of the three groups of foam breakers: solid or liquid surface-active materials other than the substance stabilising the film, liquid containing the foam stabiliser in higher concentration than it is present in the foam, and vapours of surface-active materials. In each of these groups local adsorption leads to a surface-pressure gradient and, if the spreading is fast enough and can be maintained for long enough, the film is thinned to the critical distance of 50–100 Å, followed by spontaneous breaking by mechanical shocks or thermal or diffusive molecular fluctuations. In general, the faster the molecules of the foam breaker can spread on the liquid film, the greater is the thinning and the greater the chance of rupture. For example, liquid 1,1-dihydroperfluorobutanol spreads faster on sodium lauryl sulphate solutions (4.6 cm. sec.<sup>-1</sup>) than does n-octanol (3.6 cm. sec.<sup>-1</sup>): the former material is also the better foam breaker (8). A strong solution of surface-active agent, concentrated by evaporation and drainage at the top of a column of foam, may, as further bubbles break, become sprayed over the lower bubbles, and, spreading over these lower lamellae, may well rupture them. Similarly, vapours of surface-active liquids are adsorbed locally by convection currents in the air, again leading to spreading and possible rupturing of the liquid films.

### **Anti-foaming agents—foam 'inhibitors'**

These are substances which prevent foam forming. For example, polyamides are very effective in boiler feed water, octanol is used in paper-making and in electroplating baths, while silicones, which are becoming very widely and generally used, are effective in concentrations as low as 10 p.p.m. All these substances act by being preferentially strongly adsorbed without, however, having the requisite electrical and mechanical properties to produce a stable foam.

Organic lubricant compositions are strongly foaming unless fluorinated hydrocarbons or a compound such as polymethylsiloxane is present. These materials are strongly adsorbed at the

oil-air interface and act by displacing the foam-stabilising monolayers. The rigidity of a monolayer may be destroyed completely by anti-foaming agents such as tributyl phosphate, with a concomitant decrease in surface viscosity (24). This effect is also shown by 2-ethylhexanol and 4-methyl-2-pentanol, which are effective anti-foaming agents for aqueous detergent solutions. The non-ionic reagent Span 20 (sorbitan monolaurate) prevents the foaming of egg-white, being strongly adsorbed similarly but contributing neither to the surface viscosity and rigidity, nor to the electrical double layer which might lead to liquid films of 'pseudo-equilibrium' thickness.

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## GAS AND DESTRUCTIVE DISTILLATION

By A. V. SMITH, D.L.C.

(*South Eastern Gas Board*)

DURING the past two years the research programme of the Gas Council (1, 2) has concentrated on the development of more economic methods of gas production which can be developed into large-capacity units situated near collieries, oilfields or major ports. The gas produced in these units will often be at high pressure and thus suitable for distribution via the rapidly growing grid system which may eventually form a country-wide network. New techniques for purification and distribution must be developed, the aim being to produce a non-toxic, sulphur-free fuel attractive to both industrial and domestic users.

Since vesting date the increase in efficiency of gas production has meant that the coal requirements of the gas industry have been reduced by the equivalent of  $2\frac{1}{2}$  million tons.

Coal used for gas making in 1959/60 amounted to 22,317,000 tons compared with 24,179,000 in 1958/59. The quantity of oil used for gas making continues to increase, being 750,000 tons in 1959/60 as compared with 667,000 tons in 1958/59.

Sales of gas have decreased. In 1959/60 they were 2,591 million therms as compared with 2,605 million therms in 1958/59. This decrease may be accounted for by higher mean yearly temperature, this being  $2.0^{\circ}\text{F}$  above average.

### Carbonisation

In determining the nature of the process of carbonisation of coal, a knowledge of the structure and composition of the coal itself is obviously of fundamental importance. A considerable amount of work has been done in this field and new analytical techniques have been extensively used. Brown & Ladner (3) have used nuclear magnetic resonance spectroscopy to determine the hydrogen distribution of coal-like materials and have obtained results confirming earlier work with infra-red and X-ray analysis of the parent coals. It has been suggested by Berkowitz (4) that the kinetics of weight loss curves measured at a series of constant temperatures are governed by a rate-determining diffusion process and that the decomposition reactions at any one temperature must be extremely fast. The experimental evidence is in good agreement with a simple

theoretical model. Ahuja *et al.* (5) have been concerned with the effect of reduced ring structures on the coking power of coals. From a study of chloroform extracts of coals and distillates obtained in a model still, Dryden *et al.* (6) have shown that the non-coking properties of coal are partly accounted for by the thermal instability of primary pyrolysis products. An interesting development in the study of the mechanism of coking is the use of photomicrography by Echterhoff & Mackowsky (7), who have obtained photomicrographs showing the coke, plastic zone and coke side by side. Ritter & Juranek (8) have made similar studies with a small, specially constructed laboratory apparatus in which carbonisation could be stopped at any desired time. It was thus possible to study under controlled conditions the effect of petrographic structure, rank of coal and speed of heating on the plastic state. The influence of the plasticity on the carbonisation behaviour of coal has been discussed with reference to the blending of various types of coal (9). Gyraznov & Petrov (10) have shown that in carbonisation under nitrogen gas pressure, increase in the yield of semi-coke is a function of the pressure and of the characteristics of the coal charge. By increasing the pressure, greater strength of coke from certain poor coking coals could be obtained. By adapting the Tuscaloosa oven Gayle & Eddy (11) have shown that the coking time varies as the 1.49 power of the oven width, although small changes and moderate variations of flue temperatures have little or no change on the coking properties.

### Production

The larger number of smokeless zones has led to an increasing demand for a good domestic smokeless solid fuel. Gopal *et al.* (12) have described pilot plant studies on the production of soft coke by a travelling grate stoker carboniser. Controlled devolatilisation by a restricted supply of air from below the grate gives a high coke yield of good quality. Cerchar (13) have developed a fluidised process for production of a semi-coke or granular coke of very fine quality.

As a result of a growing shortage of good coking coals an increasing volume of work is being done on the complete gasification of coal. A pilot plant is being installed in the Bromley works of the North Thames Gas Board to determine the operating variables of the Rummel twin-shaft Slag Bath Generator (14). The powdered low-rank coal is first partially gasified in the presence of steam to produce water gas in one-half of the slag bath. The residual carbon, entrained in the slag, then passes under a dividing curtain wall and air is blown through the slag to gasify the coal completely and provide the heat of reaction for water-gas production. An installation of the Lurgi process at Westfield (15) is the first of its kind

in Britain. A second installation of 45 million cu. ft./day output is planned for the West Midlands Gas Board at Colchill. In the Sumitomo process (16) coal is gasified at normal pressures with oxygen and steam and a ferrous oxide flux, and slag is separated by an upward vortex prior to being collected at the bottom of the furnace and discharged at relatively low temperatures.

The production of gas by the hydrogenation of coal or oil is an important feature of research. Birch *et al.* (17) have described the gasification of Yallourn brown coal with hydrogen in a fluidised-bed reactor and have shown that hydrogenation occurs in two stages, the first stage being fairly rapid and reaching completion when about 40% of the carbon content is gasified. The much slower second stage consists of the hydrogenation of residual carbon.

A recent development is the use of nuclear energy in the carbonisation process. The use of a powerful source of radiation (18, 19) apparently assists the decomposition of coal into gases consisting chiefly of methane. In general, however, coal has been found to be remarkably resistant to neutron and  $\gamma$ -ray bombardment (19). McGee (20) has described a joint A.E.C./U.S. Bureau of Mines research programme to determine the possibility of using nuclear heat in the process of coal gasification. This process could well be competitive with conventional methods of carbonisation and will possibly eliminate the need for compressed oxygen in complete gasification processes and also reduce coal requirements.

Research on underground gasification is still proceeding, the most effective method being apparently that of producing a reaction path by the method of electrolinking (21). An interpretation of the physico-chemical principles involved in the underground gasification of coal by air in the experimental producers in Poland has been described by Dziunikowski (22).

The use of oil and refinery gases for gas making continues to increase. At the Isle of Grain (23) the Segas process is now in full production and operations by the Shell gasification process will shortly be commencing. When the third stage is in operation the works will produce 72 million cubic feet of gas per day. A process for the reforming of oil refinery gas without the deposition of carbon has been developed (24), thus allowing gasification to be carried on continuously with a resulting increase in plant capacity of about 65%. The use of modified water-gas plant for reforming refinery gas (25) is increasingly practised.

### Natural gas

The search for natural gas in this country is still relatively unproductive, but the drainage of methane from collieries is producing a useful supplement to manufactured gas in several areas, notably the Afan Valley. This and other installations in South Wales are

described by Myhill (26). Natural gas is also being used at Whitby (27). In the absence of large deposits of natural gas in Britain the vast resources of other countries may well be utilised in this country by development of sea transport (28). The costs of importing methane and oil for gasification have been compared (29). In France, the immense reserves of wet gas at Lacq have created problems of collection and purification, many of which have still to be solved (30).

### Distribution

The transport of natural gas from Africa in large quantities for distribution into the network of mains in France has led to the consideration of a sea-bed main (31). The 500 miles of pipeline would be at a maximum depth of 9000 ft. and this would be the main difficulty, but the problems associated with this have been solved.

The problem of gas storage is almost ubiquitous. Low-pressure storage in conventional holders is expensive in space and money. Crowther (32) has described the formation of an underground cavity in a natural seam of rock salt which will accommodate 10 million cubic feet of gas (measured at s.t.p.) at a pressure of 30 atmospheres. A project for the underground storage of butane at pressure has been described (33).

### Purification

In order to produce a less toxic gas the removal of carbon monoxide is being increasingly practised (34). This results in a high concentration of carbon dioxide in the purified gas and a considerable portion must be removed in order to retain the combustion characteristics of the gas. The Giammarco Vetrocoke process (35) has been developed for simultaneous removal of hydrogen sulphide and carbon dioxide. Other methods for the removal of hydrogen sulphide include the use of an alkaline slurry of basic zinc carbonate (36) for small quantities; a moving mass of ilmenite ore containing 5% Portland cement and active carbon (37); the use of aqueous ammonia (38), and the use of materials produced in the manufacture of anthraquinone dyes from coal tar (39). The use of a suspension or solution of a copper compound in a hydroxide, carbonate or bicarbonate of an alkali metal has also been described (40).

In order to obviate siphon pumping in the long stretches of transmission mains, some of which operate at a high pressure, the drying of gas is becoming of greater importance, and a refrigeration technique has recently been developed (34a, 41).

### Analysis

With the development of increasingly efficient purification processes and more elaborate techniques for the production of gas, new and more accurate methods of analysis are required. A sensitive method for the identification and determination of organic sulphur in utility gases has been outlined (42). The chromatographic analysis of gases has become increasingly important, particularly as the ease and speed with which it may be carried out makes it an important tool in process control. Velut & Jourda (43) have described a method for automatic sampling and chromatographic analysis on two columns, one using a carbon solid phase and the other alumina and silica gels, the carrier gas being carbon dioxide.

A new technique of fractional thermogravimetric analysis (44) has facilitated the study of the rates at which various volatile components are given off during coal carbonisation and also measurement of their cumulative yields.

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